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BY
H. N. BOSE, M.Sc.,

(With fifty seven Illustrations.)

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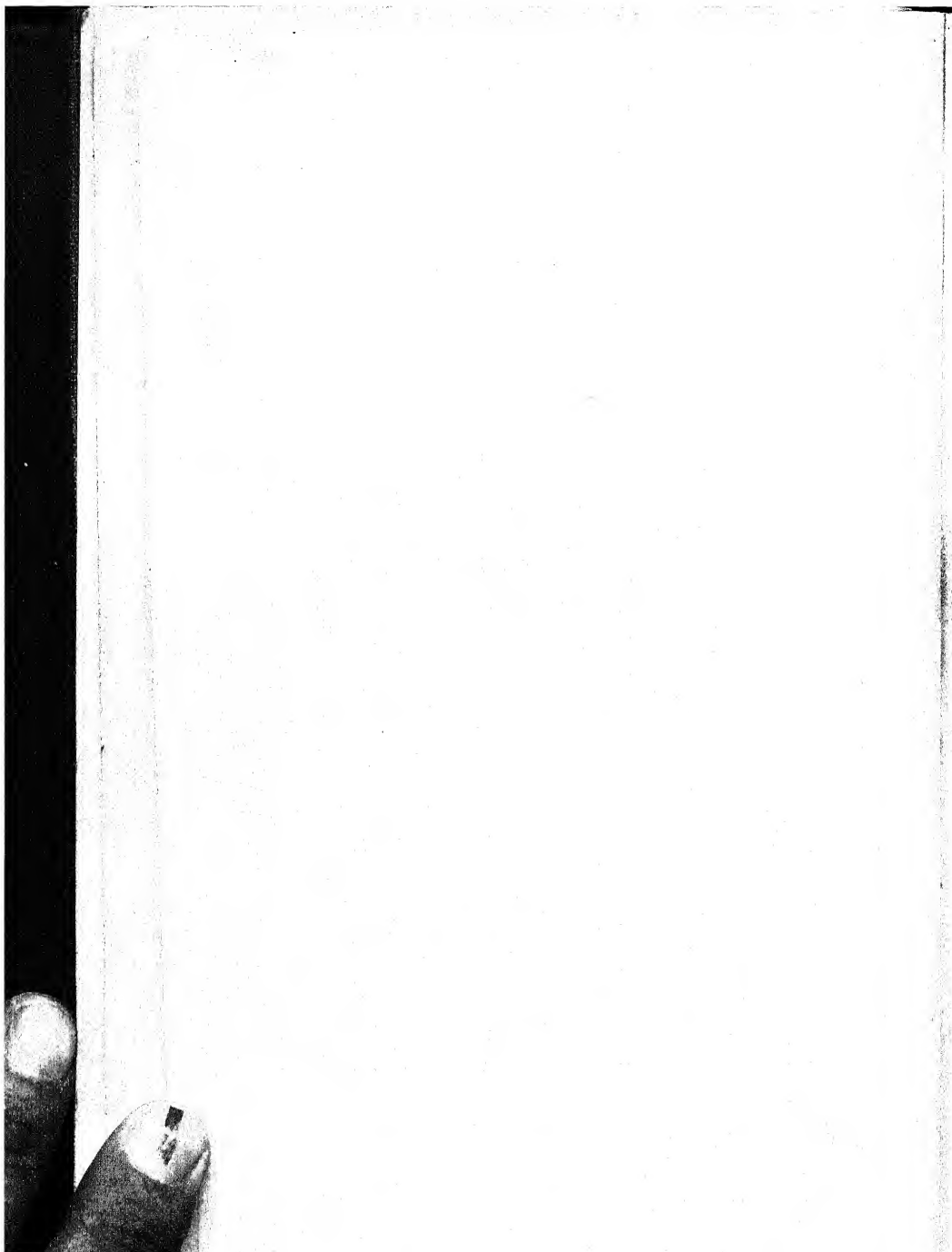
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PREFACE.

This book is mainly intended as a text book for the students of ceramics in the Universities and technical Institutions, but practical workers in this line may find this volume useful, as no pain has been spared to combine the modern theories with practical data of the various different branches of this subject as far as possible in one handy volume. The special feature of this book is the various practical formulas using Indian materials all of which have been tried by the author in the laboratories and the ceramic plant of the Benares Hindu University.

My best thanks are due to Prof. P. N. Roy of the Chemistry Department for going through the manuscript and some proof sheets, and to Mr. J. N. Biswas of the Engineering College for drawing all the sketches and diagrams used in this book and going through some of the proof sheets.

HIREN BOSE.

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CHAPTER I.

HISTORY AND CLASSIFICATION OF POTTERY.

The term *ceramic* is supposed to be derived from the Greek word *Keramic* which means the art of the potter. At the present time the term generally denotes all articles developed by heat in which clays have been used. The German and French equivalents of this term are *Keramic* and *Ceramique* respectively. In the United States of America the cement, lime, glass and enamelled iron industries are included in the term *Ceramic* but in Europe this is considered undesirable. In the present volume all branches of the clay industries only will be considered including the refractory materials where clay is used to some extent as a binding agent.

The art of pot making is the oldest of all human arts. It is naturally very difficult to trace the development of this art systematically. In the following pages attempt has been made to give only a brief history of the development of various types of pottery in Asia and Europe.

Earthenware. Perhaps the first people that used clay articles for their use, were the ancient Egyptians. Vases of terra cotta which were intended to contain provisions for the deceased, have been found in the tombs of the Memphite period (5000-3000 B.C.)- and

some bricks found under the valley of the Nile are supposed to have been made about ten thousand years ago. At later period these people also discovered the art of making glazed clay wares, the remnants of which are still to be seen in their pyramids and temples. The fine pottery of later period is most often covered with a thin glaze, coloured with sky blue or pale green. Sometimes the clay paste itself is coloured but more often left white.

Assyrians and Babylonians used terra cotta coated with various colours from very ancient times. Herodotus states that the walls of Ecbatana in Media were painted of seven colours. In the excavations made at Khorsabad upon the site of ancient Assyrian palaces, a wall was found 21 ft. long and 5 ft. high entirely faced with painted bricks, representing men, animals and trees. The specimens of pottery from Nineveh and Babylon now existing in Louvre museum in Paris are calculated to have been made as early as in 500 B.C.

The Persians, it is believed, learnt this art from the Assyrians and succeeded in improving it to a high degree of perfection. The ancient Persian pottery were made from highly siliceous bodies coated with a transparent alkaline glaze which showed much brilliance. The wares were often decorated with yellow and blue glazes with ornamentation in low relief.

In India clay products in various forms have been used since very ancient times. Recent excavations have shown that this art of potting thrived in a fairly

advanced state as early as four thousand years ago. There can be no doubt that objects found in the excavations of Harappa and Mohenjo-daro on the Indus valley are closely connected and roughly contemporary with the Sumerian antiquities dating from the third or fourth millennium before Christ. These ceramic wares have similarity with those of Kish and a seal identical with those found at Harappa and Mohenjo-daro has been discovered in the debris beneath the temple of Hammurabi's time.

Mention of pottery is made in the Vedic Hymns (2000-3000 B.C.) but the laws of Manu codified between 6th and 9th centuries B.C. are more explicit. Earthen vessels are universally used in India and potters constitute one of the great functional castes of the Hindu Social system. Much of the prehistoric pottery of India of red, brown or black tints has shining unglazed surface and is far superior in design and workmanship to the common forms of today.

Although terra cotta ware was made in India from prehistoric times, it is only during recent centuries that glazed pottery is being made here.

According to M. Rousselet the application of enamels to monumental decorations on palaces, temples and fortresses was in use from the fifth to the eleventh century, and these are found dispersed over Gwalior, Kanauj, Delhi, Chittore and Ujjain. These enamel coverings on the bricks, probably silico-alkaline, are excessively thin, very adherent and translucent. They

were often coloured with bright, and pure tones, dark or pale blue, green, yellow, orange or violet brown.

Specimens of glazed tiles after the Persian style, were unearthed during the excavations of Gour, a seat of Mahomedan kings of Bengal between the 11th and 13th centuries.

In the Punjab, the manufacture of glazed pottery dates from the period of Chengiz Khan (1206-1227). The charms of this pottery are the simplicity in shape, the directness and propriety of ornamentation and the beauty of colouring.

Hyderabad in Sind owes this art of glazed pottery to some Chinamen who were induced by one of the Amirs to settle in that district and it was from them the *kashigars* of Hyderabad claim their descent.

Chunar, Khurja, and Nizamabad, three small towns in the U. P. have developed three distinctive types of modern pottery using local clays. In Chunar, the wares are baked by a class of potters or *kumhars* from the alluvial clay of the Gangetic deposit working entirely in their homes. Merchants collect these articles from the Kumhars and then give a coating of an opaque coloured glaze on the wares by a second firing.

In Khurja, the wares are made from local red burning clay but a white coating of engobe is applied on them which forms the back ground for further decorations. A transparent glaze is then applied on the wares showing the multi-coloured decorations on the white back ground.

The Nizamabad pottery differs from the other two types as it is not coated with any glaze. The surface of the wares is made so smooth during making that it shines after firing even though not coated with any special glaze. These wares are often decorated with designs engraved on the surface and then filled with an amalgam of mercury with tin or lead.

Berhampur in Bengal and Lucknow in the U. P. have developed the artistic side of pottery to a great extent. The designs are so neat and the executions so exquisitely done that the articles can compete with the best productions of the world as far as art and designs are concerned but the quality of the material and finish leave much for improvement.

Amongst the various other types of pottery made in India mention may be made of the black and silver pottery of Ajimgarh in the North Western Province, the painted and gilt pottery of Kota and Amroha in Rajputana, the glazed pottery of Sindh and the Punjab.

These wares are generally made from clays of river deposits which are naturally impure. The first fine earthen-ware factory using white burning clay was started in Gwalior with State help by Mr. D. C. Mazumdar who had his training in modern ceramics in Japan.

The art of pottery was introduced in Spain by the Arabs and Moors. The latter people developed a new kind of ware different from the Persian one which is distinguished by its metallic lustre of the glaze. Beautiful specimens of lustrous wall tiles are still to be

seen in Spain on old Mosques. The conquest of this country by the Christians caused a rapid decline of this fine industry, but the Italians were lucky enough to have learnt this glorious art from the Moors, and carry it to their own country.

At the end of the 15th century an Italian artist Lucadella Robia, succeeded in making a new ware with stanniferous opaque glaze, which was known by the name of *Majolica*, after the name of an island called Majorca, near Spain, which was so famous for pottery during the Moorish period. The production of *Majolica* wares spread from Italy to many other countries, and at Faenza originated the French word *Faïence*, which at the present time includes all glazed pottery with a porous body similar to English earthenware.

The earliest known pottery found in Great Britain belongs to Celtic period. After Roman conquest the method of pot making was improved, but since the Anglo-Saxon conquest it again reverted to its former rudimentary stage until the 17th century. At the beginning of the seventeenth century, this industry flourished in fairly advanced stage, in Staffordshire, the chief centre of English pottery industries of today. The two essential factors, for the making of primitive pots were clay and wood, which were found together abundantly in many parts of the country, so that the potters of the middle ages were scarcely localised ; but with the introduction of coal as fuel and the ease with which both clay and coal could be found in North Staffordshire, caused the concentration of pot-workers

in this neighbourhood and by the end of the seventeenth century, it had become the greatest ceramic centre in England.

The rapid improvements in English pottery during the latter period of the seventeenth century were greatly due to foreign influence. Much credit is due to the two Eler brothers from Denmark who introduced many improvements in the technique of the industry.

Josiah Wedgwood, the most famous of English potters was born in 1730 amongst an old established family of potters. He was the youngest of thirteen children and when he was only nine years old, he started to work on a potters' wheel under his brother Thomas, but an affection in his right knee, compelled him to abandon the potters wheel and he turned to other branches of the industry. He entered into partnership with Thomas Whieldon in 1754 and the period of five years of his partnership encouraged Wedgwood to become a manufacturer on his own account. In 1759 he rented a small house in Burslem and started an enterprise which has meant so much to the pottery industry of the world. His success in cream-coloured ware, which was afterwards known as *Queens ware* obtained for him in 1765, the Royal patronage from Queen Charlotte, the wife of George III. His untiring industry and love of patient experiments, soon brought him rapid success, and in 1769 he opened the great new works at Etruria which is still under the control of his descendants. In addition to the popular *Queens ware*, the new works became famous for *black*

basalt ware, an unglazed stone ware suitable for decorative vases and figures. The *jasper ware* is generally made with a coloured ground, usually a shade of blue, with ornaments in white relief. Wedgwood died on the 3rd of June, 1795.

Wedgwood's success provoked immediate rivalry amongst his contemporaries, and in the keen competition that followed, the industry developed rapidly both in workmanship and technique. The result of this competition produced a special type of ware with a very high class boro-silicate glaze on a well burnt white porous body and generally termed as *fine earthenware*. The great success of this kind of pottery was the cause of the establishment of similar factories in most of the advanced countries of Europe and America.

The earliest pottery found in Germany and many parts of Europe were made by the Celts in the Stone Age. The technique of Italian Majolica ware found its way to Germany and other European countries in the latter part of the seventeenth century. The manufacture of Majolica appears to have been introduced into Germany from Holland by Daniel Behagel in the year 1661. This type of ware continued until about the end of the eighteenth century, when English fine earthenware so flooded the continental markets that the manufacture of stanniferous Majolica ware was gradually discarded in favour of the English plumbiferous earthenware. This new type of ware in Germany came to be known as *Steingut*.

Stoneware. In Germany a special type of pottery was developed as early as the 14th century which is generally known as Stoneware. This ware was composed of a natural buff-burning clay chiefly found in the Rhineland. Unlike the other types of ware, this new pottery has a vitrified and impermeable body glazed with salt glaze. The later developements of stoneware have produced the present day chemical stone-ware and sanitary ware, the former product being chiefly responsible for the rapid developement of the heavy chemical industry. In England salt glazing was first introduced by the Eler Brothers during the end of the seventeenth century and by the middle of the next century regular stoneware was manufactured there, using the white clay which was first discovered in England in the year 1720. In the nineteenth century the use of coloured clay was again revived due to the development and demand of chemical stoneware, drain pipes, acid jars, etc. During the present century many stoneware factories have been started in India, their main products being salt glazed drain pipes, pickle jars, sanitary wares and acid carboys.

Porcelain. As early as 200 B. C. the Chinese made a special type of pottery using only pure white clay (Kau-ling) and a felspathic stone (Pe-tun-tse). During the latter half of the 12th century the Chinese pottery was brought to Europe as an accompaniment to Chinese tea by Arab merchants who had established a regular trade with the ports of the Mediterranean Sea, specially those of Italy. In the year 1298, the famous

Venetian traveller Marco Polo used the word *Porcelain* in his accounts of China to denote their famous pottery. Gradually in later days as the specimens of Chinese pottery were introduced more and more in Europe, this term was restricted to denote a certain class of pottery having a vitrified white body exhibiting translucency, and a white glaze which has a peculiar softness quite unlike other specimens of pottery.

Finding the high excellence and importance of this new merchandise of the Far East, it was natural that the Italians would be the first people in Europe to attempt at the making of porcelain in their own country. The earliest specimen now found in the collection of the Victoria and Albert Museum in London is supposed to have been made at Florence (1575-1585) under the patronage of the great Medici family. The nature of these imitations is quite different from those of Chinese porcelain as these continental people used for their body a mixture of clay and glass evidently with the guiding principle that porcelain could only be an intermediate product between glass on the one hand and opaque pottery on the other.

The next step in this line, was taken by the French people and we are told that in 1763, Louis Poterat, a faience maker of St. Sevre near Rouen succeeded in making porcelains "like those of China" and shortly afterwards we find a similar ware making its appearance at the faience works of St. Cloud, near Paris.

This early French porcelain, was really a glass heated to a temperature insufficient to melt it completely

but enough to give it a milky transparency. Later researches of several scientists during two centuries developed the famous *Sevres porcelain* which very nearly approached the best Chinese pieces in their tender translucency and range of colour decorations.

In Germany it were the Alchemists and not the potters who sought for the composition of porcelain. In the year 1709 John Frederic Bottcher, a son of an alchemist, found a composition which was analogous to Chinese porcelain. When the news of this discovery reached Frederic Augustus I, Elector of Saxony, Bottcher was shut up in the fortress of Albrechtsburg near Meissen together with other workmen who were sworn "to keep till the tomb" the secrets they might be able to discover. Bottcher died in 1719 at an early age of thirty-five only. In course of time the products of this new fortress manufactory under different able managements became so famous in the whole of Europe, that inspite of severe strictness, various workmen managed to escape and with their help new factories were built up at several places in Germany. In 1759 and again in 1761, Frederic the Great, of Prussia, looted the Albrechtsburg and temporarily put an end to the manufactory. He had carried away to Berlin, the models, the working moulds and many of the principal workmen together with the records of works of Bottcher and his successors.

The Royal Procelain factory of Berlin owes its origin to John Ernest Gottskowski, a banker who set

up a manufactory in 1761, and here Frederic the Great sent all the materials as well as the workmen who were brought from the Meissen factory and two years later in 1763 he himself acquired the factory which became a Royal manufactory. This Berlin factory like other Royal manufactories was not a profitable business and we find that many ingenious ways were adopted to push on the sale of this Berlin porcelain.

It were the poor Jews who were forced to pay for the piper while they had no power to call for the tune. No Jew could procure a wedding certificate unless he had purchased a service set of the Royal porcelain. Moreover the Berlin lotteries had to distribute every year about fifty thousand Marks worth of these porcelains. Nevertheless when more attention was paid on the technical and scientific sides, this Berlin factory proved to be of the greatest aid for the development of the porcelain industry of the world.

Dr. Hermann August Seger (Born 1839), a great scientist, is one of the persons who are responsible for the rapid development of the German ceramic industry. He not only contributed a good deal on the subject himself, but also left a band of scholars, who are still recognised amongst the great ceramists of the world. The most important of his contributions to this industry is the pyroscope for measuring temperature inside pottery kilns and known after him as *seger cones*. In fact Seger was the pioneer who first blazed the way, along which all must travel, who hope to reach the mastery of the industry.

In the middle of the 18th century the English potters were also busy in the search for white materials to make articles similar to those of China. The first successful attempt to make true porcelain in England was that of William Cookworthy when he discovered China clay and China stone in Cornwall about 1755. Although the methods and materials for making glassy porcelain of the French type were known to these people during this period, the native potters never ceased from their independent experiments until at last a composition with bone-ash was evolved in Stoke-on-Trent just before the end of the 18th century.

This phosphatic porcelain became famous as *Bone China* and has been copied in many countries since then. The different types of porcelain evolved in different countries as mentioned before may be classified in three main groups.

1. *The felspathic or natural porcelains.* This type was first made in China and then in Germany, France and other European countries. Body is very hard and when shattered, it exhibits a distinct conchoidal fracture resembling that of a flint pebble.

2. *The Glassy or Artificial porcelain.* This was first made successfully in Italy and France and then copied in other European countries. The body is soft and distinctly glassy which easily fritter and the fractures show granular appearance.

3. *The phosphatic or imitation porcelains.* This was first invented in England and then carried to other countries. The body contains bone-ash and occupies

an intermediate position between the other two groups in their hardness and fracture.

True porcelain was never made in India prior to its introduction by Europeans. In 1839 the authorities of the East India Company directed that attempts should be made to procure efficient substitutes of English pottery in India and various clays from Colgong and other places were tested in the laboratories of the Calcutta Medical College and experiments made for glazing them. The first pottery for making porcelain was started in 1860 at Patherghatta near Colgong in Bhagalpur district of Bihar. As reported by Dr. Ball, this works "produced articles of the highest qualities, including table China, porcelain for scientific purposes, and finest Parian ware, equal to that produced in Staffordshire."

The next pottery run on modern lines was started at Calcutta during the early part of the present century. It was started and managed by Mr. S. Deb who had his training in Japan, England and Germany. The articles made here are of high order and prove the fact that high class pottery can be made in India entirely with local raw materials. In later period. other factories have also sprung up at different places of India, but the demand for ceramic wares is increasing gradually and several more factories can safely be erected to cope with the present demand.

Refractory ware. Although fire-bricks were used since the manufacture of white pottery began, the regular manufacture of refractory ware commenced in

the 19th century. It is said that this industry first originated in England but the continental manufacturers have made a rapid progress in this line during recent years.

In India fire-bricks were made by Messrs. Burn & Co., established in 1859 at Raniganj in Bengal. In 1875 some fire-clays were tested in the furnaces of the Calcutta Mint where several of them stood the test perfectly. The Jubbulpur works of this company were established in 1890 and for many years fire-bricks made by this company, the only one of the time, specialising in this line in India, were supplied to furnaces and foundries of railway works. With the establishment of the Tata Iron and Steel Works in 1909 near Jamshedpur the demand for high grade fire-bricks and other refractory goods increased so rapidly that several other concerns have been established today who make different types of high temperature refractory wares utilising Indian raw materials.

Classification of Pottery. With the introduction of different types of pottery wares from time to time, it became necessary to classify various products into groups having the same characteristics.

Brongniart divided all pottery ware into two classes soft and hard, according as their bodies are capable of being scratched by an iron or not. The hard ones are again subdivided into two classes opaque and transparent. These three groups are again subdivided into nine others according to the chemical composition of the body and the glaze.

Salvetat proposed to base a classification on (a) pottery without a glaze ; and (b) pottery with a glaze ; and to subdivide these classes into opaque and transparent wares. Further subdivisions take to account the composition of the body and the glaze.

Bourry classed pottery into (a) permeable, and (b) impermeable wares and further subdivides them into five groups according to the nature of the body and glaze.

Following Bourry's classification the present author prefers to divide all clayey wares into the following five groups.

Terra Cotta. This term means 'baked clay' and at present denotes all pottery ware with a porous body and without a glaze. These wares are generally made of red or buff burning clays fired at comparatively lower temperatures than wares of other groups.

Earthenware. This division includes all permeable pottery made of white or coloured clay, but always with a coating of glaze on them. This includes the faience of France, steingut of Germany and all such wares known as majolica, iron stone, flintware, etc. and the so-called Rockingham ware, made of red burning clay and covered with a brownish black glaze.

Stoneware. These are vitrified and opaque pottery either made of white burning or coloured clay. The white wares are often covered with a glaze like porcelain but the coloured wares are generally salt glazed.

Porcelains. This group includes all white, impermeable clay ware generally covered with a similar glaze, and translucent when sufficiently thin.

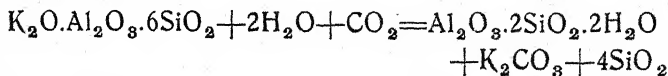
Refractory wares. This kind of ware is made either of clayey materials, such as fire bricks, saggars etc. or from substances free from clay like silica bricks, graphite crucibles. These wares are not covered with a glaze. They are fired generally above 1400 degrees Centigrade.

CHAPTER II.

RAW MATERIALS.

Clays. The term clay (Argile in Lat.) is applied to those fine grained earthy materials composed of various minerals whose most prominent properties are—(1) Plastic when wet. (2) Capable of retaining the shape when dried. (3) Formation of a hard rocklike mass without losing the original contour when heated to red heat.

Formation of clays. Clays are decomposition products of igneous rocks containing mainly alumina and silica which by the action of the weathering agencies are converted into plastic or semiplastic masses. When the parent rocks contain impurities like lime, magnesia, iron etc., the final products are the impure clays, but if the disintegration takes place from felspathic rocks the residual clays are comparatively pure and we get white clays known as *kaolins*. The precise manner in which this decomposition occurs is still open to investigations. The reactions which occur are so complex as to be only very imperfectly understood. One of the simplest means of representing what occurs is by the following equation. This process of decomposition of rocks into clays is known as kaolinization.



The potassium carbonate is leached out by rain water and the silica remains mixed up with the clay as we find in almost all clay deposits.

The principal hypotheses advanced to explain the modes of formation of kaolin embrace the actions of :—

- (1) Surface weathering.
- (2) Waters descending from swamps and bogs.
- (3) Ascending waters containing CO_2 .
- (4) Sulphuric acid solutions and hydrogen sulphide.
- (5) Hydrolysis.

Surface weathering as a cause of kaolinization is the oldest explanation and still finds a place in all text books on geology. The depth to which the surface decomposition of rocks may descend is very variable. In certain regions specially beneath old established forests, it may go to great depths: in exposed tracts of rocks it may be non-existent. It will obviously be influenced by the character and amount of jointing, by the nature of climatic conditions and by the texture and mineralogical features of the rocks. What cannot fail to strike the observer is the limitation of the areas over which white residual kaolins are found compared with the wide extent of rocks from which these clays could be formed. We now know that normally this agency does not produce white kaolin; the common weathering products of granite and other felspathic rocks are indeed quite different in their characters, as surface weathering results from the actions of weak acids and the process is an oxidising one, which increases the total content

of iron and magnesia in the subjacent rock. Where a kaolin deposit appears to have been due to surface weathering, it is possible that bog waters may really have been the cause though the evidence of its existence may have been removed.

The ground water beneath swamps and bogs does seem to be capable of yielding a white kaolin from felspathic rocks but the process does not seem to be capable of indefinite downward extension. It is in Germany, however, that the association of kaolinised igneous rocks with brown-coal beds has given rise to a strong belief in the efficacy of these beds as inducers of kaolinization. Most of those who support the swamp water theory do so on the grounds that these waters containing organic matter, humic and related acids, and carbonic acids are reducing in their actions and tend to decrease the total content of iron and magnesia in the subjacent rock. The reddish and grey colour observed in some kaolins, such as Halle kaolin, are due to organic staining, which can be driven off by heating. These stains might be introduced from moor water but could not be produced by post-volcanic processes.

The high content of alumina in kaolins is an indication of less mechanical and disruptive action than what takes place in weathering, whereby much clay substance is washed out and excess of silica left behind.

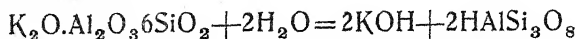
Ascending waters, containing carbon dioxide appear in limited cases to have been the cause of local kaolinization. This explanation cannot however be applied

to the majority of kaolin occurrences. Gagel and Stremme have described the kaolinization of the granite at the Giesshubler spring near Karlsbad as an example of this process. In this case and also in another at Canical in Madeira the iron content of the original granite was removed from some parts and concentrated at others but the content of potash, soda and lime had been considerably reduced. According to Stahl the green tint of moor kaolins and also the greys and browns due to humus substances are not seen, as a rule, in kaolins formed by acid spring waters.

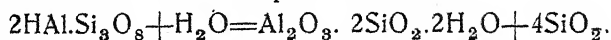
The action of sulphuric acid bearing waters may have been instrumental in producing kaolinization in certain cases. If these solutions were ascending there is less difficulty in understanding their actions than if they were descending, for in the latter case it is not clear how the kaolin would be freed from iron stains. It is known that sulphuric acid in weak solution will attack feldspars and it is quite possible that it could be an effective agent of kaolinization in this form but the whole evidence in support of this theory needs more thorough examination.

There can be no doubt that hydrolysis is a very important factor in the decomposition of feldspars in nature; but associated with simple hydrolysis there must be some means of removing the basic products. That orthoclase is dissolved by water and hydrolysed, is shown by the fact that it yields a solution alkaline to phenolphthalein, litmus and similar indicators. If we

assume for clearness, ideal formulæ, this may be expressed thus :



The potassium hydrate thus formed may unite with CO_2 to form carbonates or bicarbonates, or with other acids, forming salts more soluble than the orthoclase or the hydrolised acid thus formed— $HAlSi_3O_8$ which seems to be unstable under ordinary conditions. It splits off in greater or less amount forming kaolin and silica in the form of quartz or sand.



In the decomposition of the orthoclase, some of the potassium hydrate formed, may well be expected to react with kaolin to form muscovite.

Kaolin, like many other substances, may be formed by any one of several processes in all of which water hot or cold, and carbonic acid take part. From a technical standpoint the most important are the moor-kaolins for their low iron content, the iron being reduced and leached out. In the kaolins formed by other processes where air is not excluded, the iron readily separates out as a colloidal hydrate and thus lessens the value of the kaolin.

Clays may be broadly divided into two groups :—

- (a) *Primary* or residual clays; Laterite, kaolin or china clays etc.
- (b) *Secondary* or transported clays; Fire clays, ball clays, shales, loams, loes etc.

The residual or primary clays are those which are found on the original beds where they were formed

by the decomposition of the parent rocks. They vary widely in colour.

When the residual clays are removed by transporting agents such as water, ice, wind etc, and deposited at lower levels, they are called secondary or transported clays. These transported clays are usually, but not always, less pure than the residual or primary clays. The secondary clay deposits are generally formed by sedimentation, hence these clays can be distinguished from the residual clays chiefly by their stratification and also by the fact that they commonly bear no direct relation to the underlying rock on which they may rest.

Laterite. This represents a peculiar type of residual clay formed by the weathering of bauxitic rocks yielding a product in which silica has been largely eliminated and aluminium and iron hydroxides predominate. The changes which bring about its formation appear to be peculiarly characteristic of the tropics.

Two typical analyses of residual laterite are given below. The first one is of American origin and the second one is from Nalhathi in India. In India lateritic clays containing very high proportions of iron are known as *Morum* and are chiefly used in road making. They are very sticky when wet but become quite hard when dried up.

SiO_2	...	35.14	38.2
TiO_2	...	0.7	—
Al_2O_3	...	40.12	43.38
Fe_2O_3	...	4.12	2.12
CaO	...	0.45	4.43

MgO	...	0.21	0.53
H ₂ O	...	17.84	11.85
Insoluble matter	...	1.48	—
<hr/>			
Total	...	100.06	100.51

Kaolin. The name Kaolin is a corruption of the Chinese word *kauling* which means high ridge and also is the name of a hill near Jauchau Fu, from where the clay used for making porcelain was obtained.

The term is now generally applied to those residual clays usually white in colour and derived from rocks composed entirely of felspar or other similar minerals, containing no or very little iron oxide. These clays contain a high percentage of the mineral *kaolinite* together with other hydrous alumino-silicates. In England the term *china clay* is applied to the white plastic clays derived from washing the decomposed Cornish or Devonian granite. In America, however, the term kaolin has been stretched to cover certain white sedimentary clays like those obtained in South Carolina and Georgia. But for all practical purposes kaolins and china clays may be taken as identical containing approximately 46 p.c. silica, 40 p.c. alumina and 14 p.c. water, and corresponding to the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

Washing of kaolin. Kaolins as mined are rather siliceous and mixed with a great amount of undecomposed rocks. These siliceous matters have to be separated by a process of washing with water before the clay can be used. Two different methods as

followed in England and Germany for washing kaolins are given below :—

English method. The chief clay deposits of England lie on the south western part of the country and the counties of Devon and Cornwall are chiefly famous for their rich clay deposits. The clay beds lie generally between 10 to 20 feet under the surface soil known as 'over-burden' which has to be removed before the clay can be obtained.

The decomposed rock containing kaolin is loosened by hand rake or blown up by dynamite and the clay contained in it is washed down by powerful jets of water. Since different veins contain different kinds of clay, it requires some experience to work judiciously separate veins and mix them together to keep up the standard quality and colour of the clay.

All these washed clay streams collect into a main channel which empties itself into a shallow tank situated inside the pit and called "sandpit", where all the heavy portions of the suspensions are deposited. The clay-water is then pumped up to the surface of the ground, and it still retains a considerable amount of very fine sand and a good deal of mica in suspension. Here the clay stream is joined with another stream of fresh water to dilute the suspensions and increase the speed of the clay stream so that the least amount of suspended matter is separated during the long run in open channels to the 'micas' or places, where clay streams from several mines join together and deposit the fine particles of sand and mica. The liquid in these

streams generally contains about 3 p. c. of solid matter.

The 'micas' are long shallow vats about 200 ft. in length and divided into five or six sections, each section being a step lower than the former one. Each section is again divided into narrow channels about 18 to 20

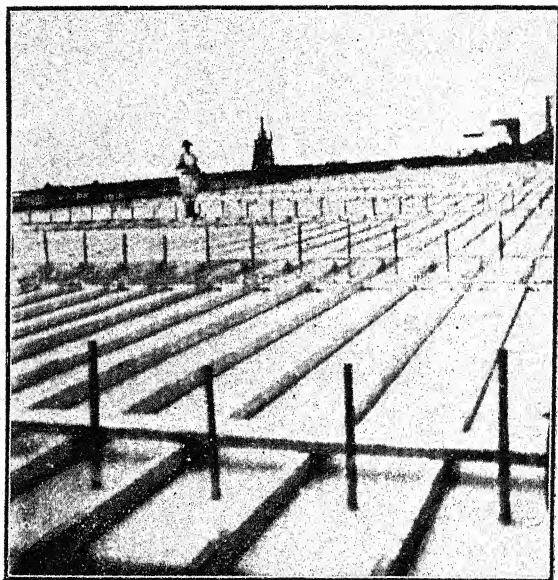


Fig. 1. Micas in an English mine.

inches wide and a foot deep. The stream of clay water runs through these channels very slowly with a speed of about fifty feet per minute which can be regulated according to the fineness of clay required at the final stage. At the entrance of the 'micas' there is another tank called "rough drags" about 25 ft. long, 10 ft. to

12 ft. wide and 3 ft. deep. Here all fine sands are deposited before the clay stream enters the 'micas' where only fine particles of mica and the coarser particles of clay are deposited. These deposits amount to about 20-30 p. c. of the weight of clay produced and are used in various industries, such as paper, paints and cotton mills.

The water containing the clay now runs into the clay pits which are circular cement lined wells tapering downwards towards a hole at the bottom about one and half inches wide which can be regulated according to the richness of the clay slip required. These pits are 15 to 20 ft. in diameter and about 10 ft. deep. There are series of holes on the side of these wells through which clear water can be run out as the clay settles. This water is used in the mines again.

The clayslip from these settling pits generally contains about 25 per cent of solid matter. This slip is now allowed to flow down to the drying plants which are generally situated near the port of shipment. One of the pipe lines carrying this clayslip runs about five miles with a fall of 1 in 400 and a diameter of 12 inches. Near the drying plants the clay slip falls into large rectangular settling tanks where the clay is allowed to settle and the accumulated water is run out from the sides of the tanks. The clay is now sufficiently thick and contains about 50 per cent of water.

The mud is now placed on open hearths called 'dry pans' which are built along the sides of the settling tanks and at a slightly lower level so that the clay can

be conveniently transported on trucks from the tanks to the floor of the pan. These dry-pans are built of fire clay slabs and are about 120 ft. long and 20 to 25 ft. wide. The heat is supplied by a furnace placed at one end of the pan and the hot gases are carried

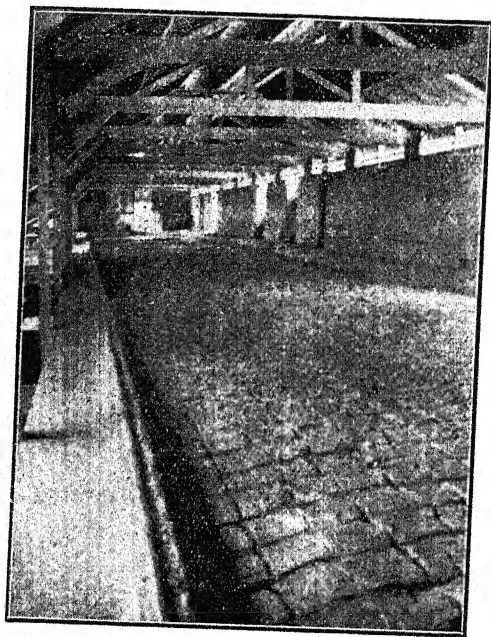


Fig. 2. An English Dry-pan
through flues running below the surface of the pan and connected to a stack at the other end. The clay is spread on this hot pan six inches thick and when sufficiently dried the clay is taken out in small blocks. The water content of this dried clay is about 8 to 10 per cent.

German Method. The method of winning kaolin followed in Germany is more mechanical than that of England. In that country the kaoline rock is mined by mechanical power and carried on trucks up to the store-room from where the material is delivered into the vats of a horizontal blunger having perforated sides. In this blunger the material is pulverised under a continuous supply of water and the clay-milk flows out through the holes of the blunger which retains the coarser materials which can be occasionally discharged out.

The clay milk leaving this blunger enters a tank where the coarse grained sand is allowed to deposit. This sand is removed from the tank by means of a wheel with perforated buckets which empty the sand into a car by which it is carried away. From this smaller tank the clay milk falls into two bigger tanks, situated side by side where the speed of the stream slows down and the fine grained sand is deposited. The sand is removed from these tanks from time to time by hand rakes.

From the upper borders of these sand-tanks, the clay water enters a system of wooden grooves similar to the 'micas' of English plants in which the finest sand and the particles of mica are allowed to settle down and are occasionally removed.

The clay milk then enters the settling tanks where the clay is allowed to settle down. The clear water is drawn off by means of a syphon pipe into the water tank and from there it is pumped back to the fresh water tank near the store room.

The clay mud is pumped from the settling tanks into the filter presses where the clay is compressed into stiff cakes which are then dried on wooden racks heated by steam pipes.

The whole plant is projected in such a way that its out-put can be increased by installing another filter press.

In Indian clay mines, where the annual output is very small, the method of winning the clay is much simplified. The decomposed granite rocks are quarried and powdered by hand labour. The powder is then blunged with sufficient water to wash out the clay material from the accompanying grit. The clay water is then run in long narrow channels in order to allow the heavy suspensions to settle down, after which the clay is allowed to settle in small settling tanks. In moderate works the clay slip from these tanks are pumped and pressed into cakes in iron filter presses but in small ones, the mud is dried in open sun or in plaster troughs.

Some clays, which when washed retain a faint tinge of yellow, are treated with a solution of aniline dye in order to decolourise or neutralise the yellow. For this purpose a 'blue-house'—a small shed, is erected over the channel leading from the micas to the settling pits, and a syphon or other arrangement is made to drop the blue solution at a regular rate into the clay stream as it flows past.

Purification of Kaolin. At Karlsbad a new method of refining kaolin has been introduced,³ utilising the

results of researches conducted by V. Schwerin. It is based on the principle that when suspended in water, particles of most of the clays possess a negative charge, whereas quartz, pyrites and other impurities associated with clays have either an electric charge much lower than clay particles or possess an opposite charge. Hydroxyl ions raise the migration velocity of the negatively charged clay particles to the positive pole. Soluble salts when present in clays complicate the result. This principle has been utilised in practice by the firm Electro Osmos Ltd., situated in Chodov near Karlsbad, in Czechoslovakia.

The kaolin is mixed with about four times its weight of water and thoroughly blunged with the requisite amount of sodium silicate solution which makes the clay mud thin. It is then allowed to flow through narrow channels where the coarser impurities settle down. The liquid suspension is then led into a settling vat where a small quantity of mud consisting of coarser particles of clay is collected but the major part of the suspension flows into the osmos plant where through the action of electric current on the kaolinic suspension the finest particles of kaolin deposit on the anode as a thick slime whereas the impurities remain in the water or collect at the kathode from where they are removed by means of a continuous worm.

The apparatus consists of a cylinder of lead which revolves slowly on a horizontal axis within a trough which receives the clay slip, the lower portion of the cylinder being immersed in the slip. Round the

immersed part of the drum there is a semi-circular kathode of brass gauze, the cylinder itself serving as the anode. The clay slip is made to flow slowly between these two poles in a perpendicular direction to that of the current from a D. C. supply of 110 Volts at 0.01 Amp. on the sq. cm. There are two wooden agitators

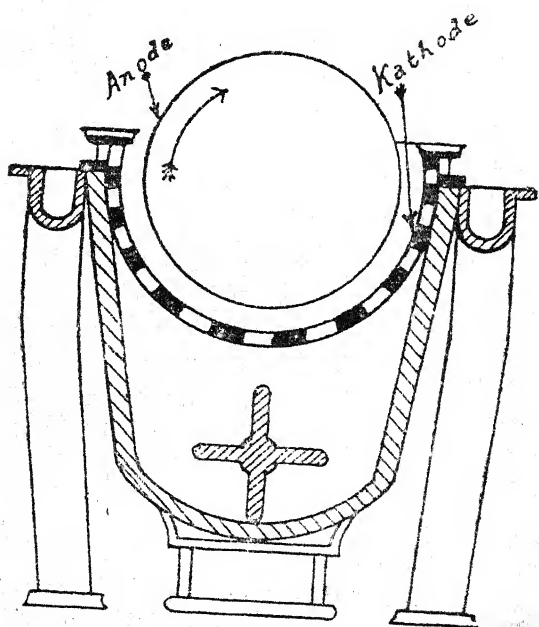


Fig. 3. An Electro Osmos plant.
inside the trough in order to avoid any sedimentation taking place inside the trough.

A thin layer of about 10 m.m. of pure clay substance with 20 to 25 per cent water deposits on the surface of the drum which is scraped off by means of

a suitable knife and charged into trucks and conveyed to the filter press where it is pressed into cakes for drying. The drying is carried in tunnel driers.

The water leaving the Osmos plant is used again for washing purpose. One apparatus can deliver daily 9000 kilos of kaolin of very high quality. The current consumption is 200 K. W. per hour.

Instead of this type of rotary apparatus, special filter presses can also be used for the same purpose. These are arranged in the usual manner with the difference that the discs carry anodes of hard lead and kathodes of perforated brass plates and insulated leads for current supply. The filter cloths are stretched only over the kathodes. The suspension is pressed into the filter press by means of a pump, the speed of inflow of the kaolinic suspension corresponding to the outflow of the liquid exempted. As soon as the filter press is completely filled up and the amount of water in the clay becomes about 20 per cent the current is cut off, the press dismantled and the clay cakes taken out. These osmotic filter presses do not work under high pressure and are therefore of lighter design. A filter press consisting of fifty chambers of 1 sq. meter surface, drains 25 tons of clay daily, the current consumption being 18 K. W. hours per ton.

The effect of this elaborate process of purification can well be judged from the following analyses of two samples of kaolin both before and after purification.

	Raw Kaolin. (Ignited).		Purified Kaolin. (Ignited).	
	A	B	A	B
SiO_2	71.23	62.52	55.12	52.90
Al_2O_3	19.55	35.93	42.90	45.50
Fe_2O_3	1.79	1.35	1.59	1.16

The softening temperatures of the clays increase by about 60° to 80° C after purification.

Classification of Kaolins. Ordinary washing process does not deprive natural kaolins of their accompanying impurities and according to the presence of these impurities kaolins are graded as follows :—

(1) Pure Kaolins ; do not contain more than 5 p. c. of free silica and 2 p. c. of fluxes. After firing, the best qualities form a mass of milky whiteness. They are used in the manufacture of porcelain and fine earthenware, and in several non-ceramic industries.

(2) Alkaline Kaolins; may contain about 5 p. c. of alkalis derived from felspar and mica. The proportion of iron may be up to 2 p. c. They can be purified by very careful washing which removes the greater part of the alkalis, but are inferior to the clays of the first group. These clays are used for making earthenware and fine pottery.

(3) Siliceous Kaolins; contain up to 25 per cent. of free silica in the state of impalpable powder. These

clays are not very plastic as can be judged from their composition and are used in the manufacture of porcelain and certain kinds of faience, where a very plastic body is not required.

(4) Alkaline Siliceous Kaolins; contain a considerable proportion of both alkalies and silica. They partake of the properties of the two preceding kinds but are less refractory.

(5) Ferruginous Kaolins; contain a considerable amount of iron oxide which prevent a white body being produced on firing. They are chiefly used for the manufacture of refractory materials provided they do not contain too much alkalies. Kaolins with high lime content are known as calcarious.

Properties of Kaolin. The physical and chemical properties of china clays or kaolins may be considered as those of the almost pure materials, for on account of the various impurities present in the common kaolins their properties vary considerably. The colour of kaolins and china clays vary from white, cream, to pale grey on account of the presence of vegetable matters but on firing these organic colouring matters must go leaving a quite white mass. The colour of china clays may be considerably modified by the presence of tourmaline which tends to give a bluish tinge of greater or less intensity. The presence of small amount of iron in china clays imparts a cream colour which becomes more apparent after firing. The softness of kaolin is very characteristic as also the soapy touch. The texture of kaolins and china clays is that

of a lump of immeasurably fine grains which can easily be rubbed to powder. To the naked eye china clays appear structureless, but under the strong microscope they seem to consist of small flakes or scales. The plasticity of china clays is very low compared with other highly plastic clays, the most important amongst which are the ball clays of England, which are very plastic on account of their extremely fine grains and presence of organic substance and soluble salts. The fineness of a properly washed kaolin should be of such an order that the whole of the material should pass through a sieve with 200 meshes per linear inch, and at least 90 per cent should be carried away by a stream of water flowing at the rate of about 2 feet per hour.

Kaolin has a peculiar property of absorbing and retaining colouring matter and soluble salts. China clay is not affected by dilute hydrochloric acid, but it is decomposed by prolonged treatment with boiling sulphuric acid. The so called rational analysis of clays propounded by Seger and so much followed in Germany is based on this behaviour of China clay with strong sulphuric acid, but Mellor of England gives the following reasons against the general adoption of the above method. Mica is a constituent of some clays and fine dusts of this material are practically all decomposable by strong sulphuric acid; also it is hardly possible to dissolve the 'clay substance' without some loss of felspar present in the clay. The treatment with sulphuric acid affects even the quartz particles to some

extent and leads to their removal by the subsequent alkali treatment.

When heated to 800° to 900° C china clay is converted into a hard porous mass with a light pink colour, easily attacked by acids. The pink colouration is due to the separation of the iron in the clay as free ferric oxide. When heated to 1100°C a good sample of china clay is pure white, very hard, not vitreous, but close in texture, and does not readily absorb much water though to the tongue it feels porous. It ceases to be attacked by acids at this stage.

For all practical purposes, the pure china clay may be regarded as infusible, its softening temperature being above cone 35 (1770°C). If either lime or silica is added to pure clay in any proportion the melting point of the mixture is lowered. In large masses such as bricks, china clay has a higher refractoriness on account of the slow rate at which heat penetrates the mass. China clay alone is unsatisfactory for making furnace linings etc., for its lack of cohesion, and bricks made of it cannot long resist repeated heating and cooling, and the corrosive action of fine dust.

When heated to 110°C commercial china clays lose about 5-6 per cent of moisture; on further heating to about 600°C the *water of combination* begins to be liberated which seems to be complete at about 800°C. At about 900°C the anhydride breaks down to free Al_2O_3 and SiO_2 . On further heating to about 1100°C the silica and alumina combine to form *Sillimanite* ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) but above that temperature a new compound is

formed which Mellor and Scott (1924) named as *Keramite*. Bowen and Greig state that the crystals which have been called sillimanite are composed of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and they call it as *Mullite*. This mullite begins to form at temperature 900°C in the amorphous state but as the temperature rises above 1300°C the mullite begins to crystalise.

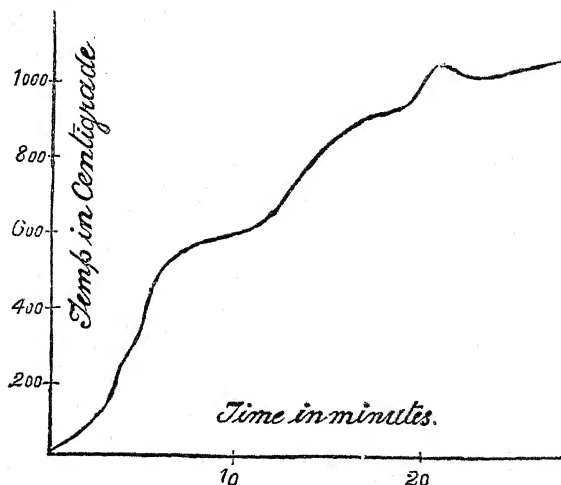


Fig 4. Heating curve of Kaolin.

If a graph be plotted to indicate the rise of temperature on heating kaolin, it is found that the temperature does not rise uniformly. Near about 600°C the curve flattens for sometime showing that the heat applied is absorbed in breaking down the water of crystallisation of kaolin. At about 900°C the curve flattens down again when the anhydrous clay breaks up into free Al_2O_3 , SiO_2 and Fe_2O_3 . At higher temperature the

curve suddenly rises up showing an exothermic reaction probably due to the combination of Al_2O_3 and SiO_2 to form sillimanite or mullite. In case of impurities present in the clay these characteristic changes are less easily recognisable.

Uses :—China clay is used, besides the manufacture of pottery, in paper making, in filling of calico, in the manufacture of alum, and ultramarine. The fine mica separated from the china clay in the washing is used for weighting coarse papers, paper boards etc.

Secondary clays. Secondary clay deposits are found not on their places of origin but the clays are transported to their present beds by some natural agencies. These clays are in general more plastic than the primary clays on account of the physical and chemical changes they have under-gone during the course of their transportation. There are several varieties of secondary clays found in nature but those mainly used for pottery industries can be divided broadly into three different groups depending on the manner in which the clays resist the action of heat.

(1) *Refractory clays*. These are distinguished by their nature of withstanding high temperature of firing. Strictly speaking all pure residual clays come under this head but the most important members of this group are termed as fire clays which are coal-measure shales with high fusion point. It is not safe to express the refractoriness of a material in terms of temperature alone, unless the conditions under which the said material can withstand such high temperature are also

stated. Thus, an acid refractory material, such as silica, will be destroyed rapidly if heated in contact with a base such as lime. Also a refractory brick which can stand a very high temperature without any load, will give way far below that temperature when heated under a heavy load. For our purpose, we shall call that material as refractory which shows no external sign of fusion when heated up to 1580°C or Seger cone 26, under an oxidising atmosphere and in such a manner that the temperature rises during the heating at a rate of about 10°C per minute.

Many attempts have been made to find out a relationship between the refractoriness of clays and their chemical composition but these have not yet been quite successful except with very pure clays. Bertrand made several experiments to find out the relationship between the percentage of alumina and the refractoriness of clays, but could not establish anything definite beyond the fact that clays containing a high percentage of alumina are the most refractory.

The most successful attempt made in this direction is that of Ludwig, who assumed that the fluxes in a clay are in the form of a solid solution with the clay as solvent. He arranged the composition of a clay in the form of a formula with alumina as unity, $-x\text{RO}, \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2$ where RO represents the total bases. By plotting x as ordinates and y as abscissæ, he obtained a chart in which diagonal lines were drawn representing the limits of Seger cones, so that a certain clay composition falling between any two such lines will

fuse between temperatures indicated by Seger cones marked there on.

This chart, helpful as it is for the more refractory clays, is not so reliable if the total bases RO exceed 6 per cent. The reason for the failure of this chart in many cases is that the fire-clays are not homogeneous materials and the fluxes are not distributed uniformly throughout the mass to be treated as in solid solution. This chart also shows, and it is confirmed by practice also, that the addition of silica and of

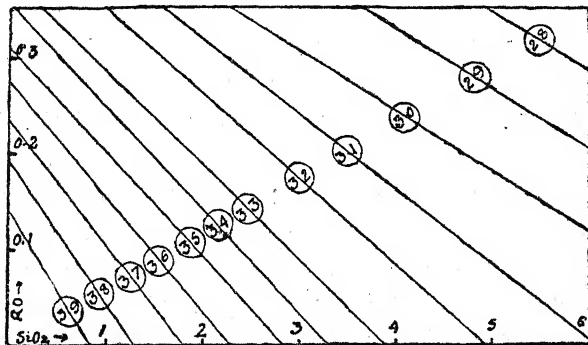


Fig. 5. Ludwigs chart.

almost any metallic oxide except alumina, will reduce the refractoriness of a fire clay, but if the added material is very coarse grained its influence will be less marked than if it is in the form of a fine powder.

Fire-clays are a class of plastic refractory clays and are generally found beneath the coal seams. These clays vary greatly in composition, from an aluminous clay to a highly siliceous one, and are used for making refractory materials for various purposes.

The fire-clays are generally greenish grey in colour, compact, dense, and of varying degree of hardness. On exposure to the weather they usually crumble down, and on absorption of moisture, become converted into plastic clays. It is believed by some geologists that these clays formed the old soils on which grew the plants which later formed the coal seams. From these ancient soils the alkalies have been removed by the growth of vegetation ; but other authorities contend that true fire-clays originated from the oxidation of the lower part of the coal seams, for, they say, that coal ash appears to consist very largely, of calcined clay. They further argue that if the under-clays were soils originally, the lower part of the bed ought to be richest in lime and other bases, and to gradually rise to purer clays ; but this is not the fact.

Fire-clays from various parts of the same seam are by no means alike. Broadly speaking, they are all aluminosilicic acids richer in silica than the kaolins but poorer in alkalies than ball-clays, and usually containing free silica together with other impurities which have a great influence on the properties of the clay.

In judging the quality of a fire-clay, chemical analysis is of little value, except the knowledge of the percentage of total fluxes, silica and alumina. The refractoriness should be judged by heating tests, for which the clays are made into small three-sided pyramids whose height is at least four times as great as one side of its base. These are placed inside an experimental furnace together with other standard

Seger cones in order to judge the temperature when the testpyramid bends down.

There is a marked relationship between the plasticity and refractoriness of a fire-clay. Those clays that dry to a hard and tough mass vitrify on firing, much earlier, forming dense impervious bodies. These clays are used for making glass-pots in preference to the highest refractory clays as they easily acquire great density due to their high plasticity, and are less attacked by molten glass. Moreover, a clay which is less heat-resisting than another, may yet be superior in its general durability for some industrial purpose if it possesses a greater resistance to corrosion by slags or to abrasion by flue dusts.

Marls are naturally occurring mixtures of clay with large proportions of chalk or limestone powder. This term is also used in a misleading way specially in Great Britain, to denote ordinary fire-clays of average refractoriness found in abundance in that country and chiefly used for making saggars and low grade fire bricks.

Flint fire-clays. These are highly aluminous flint-like hard clays used only after grinding in ball mill.

Refining fire clays. Iron present in clays and reported as Fe_2O_3 by the analyst is largely present as pyrites or sulphide (FeS_2) and siderite or carbonate (FeCO_3); only small portion may be present as oxide (Fe_2O_3). These impurities can be classified under three groups according to their sizes :—

- (a) Particles coarser than 200 mesh.

- (b) Particles between 200 and 350 mesh.
- (c) Fine particles down to the colloidal state.

The first group of particles make black or brown specks on the refractories and when the refractories are used in the furnace these impurities form slag and give way. These can be separated by an electromagnet. Very high magnetic intensity is necessary for this purpose. Iron impurities are very weakly magnetic, pyrites being 0.23 per cent and siderites 1.82 per cent as magnetic as pure iron. It has been found out that the optimum magnetic permeability in these particles is developed when the clay has been pre-fired at 400°-600°C and then very finely ground. The degree of magnetic susceptibility varies directly with the fineness of the particle. The clay is calcined in rotary furnace fired with producer gas.

When clays containing iron compounds of the size of group (b) are fired, these particles fuse at a much lower temperature than the remaining mass and spread out to form small patches many times as large as their original size, spreading in the same way as drops of ink on blotting paper. These impurities can be removed by the method known as *film floatation*. Similar process is generally used in concentrating such ores as sulphides and carbonates of nickel, copper or lead. Iron compounds are also affected by this method. On addition of certain floating agents like pine oil, creosote oil, kerosin etc., to a slurry containing these minerals a surface action is developed which causes the mineral particles to float on the surface as a scum

from where they are skimmed out. The clay or sand particles are unaffected by the oily emulsion and remain at the bottom. For one ton of clay, 400 gallons of water and one pint of a mixture of kerosin oil and creosote oil in equal proportions can be used.

The impurities of the size (c) are mostly oxides of iron and so uniformly distributed throughout the mass that they are not separated by any commercial method. On firing such a clay, the whole mass is coloured ivory or brown.

Occurrence in India :—

1. Ranigunj coal field in Bengal.
2. Western side of the Rajmahal Hills and Patharghatta in the Bhagalpur dist. (Behar).
3. Rajahara in the Daltonganj coalfield in Behar.
4. Katni and Jubbulpore in C. P.
5. Umaria in Central India, Gollahali in the Bangalore dist. Mysore.
6. Umaria Sawai in the Khasi and Jainti Hills, Assam.

(2) *Vitrifiable clays.* Vitrifiable clays are those which become vitrified or partially fused at porcelain heat—1350°C. They contain a higher proportion of fluxes than the refractory clays and serve as a base for the manufacture of artistic stonewares, sanitary wares and for chemical industries.

Ball clays are pure and very plastic secondary clays specially found in England which vitrify but do not lose the shape at porcelain heat. For these properties these clays are used in conjunction

with other clays for making white earthenware and stoneware. Some of the ball clays of Dorset and Devonshire are sufficiently resistant to heat to be classed as refractory clay. Geologists are of opinion that this clay was originally washed out from the granite hills, deposited in the lower regions of the country and finally embedded under the surface soil. The dark colour of the clay is chiefly due to the presence of organic impurities and charred vegetation. Big blocks of lignite or charred wood, fairly advanced to the way of becoming coal, are often dug out with ball clays. These are to be separated by hand picking. The clay mines at Devonshire are generally from sixty to eighty feet deep and they are worked by digging a shaft down to the bottom and then cutting the clay by hand spades. The clay lumps are piled high near the mouth of the pit and left to 'weather' under the actions of frost and rain. It is claimed by some old miners that one night's frost and rain do more good to this clay than years' storage under cover. During hot seasons they generally sprinkle water on the clay heaps to keep them moist. The ball clay is used in pottery, direct from the mines without going through any preliminary washing treatment.

In chemical composition, the ball clays do not differ greatly from the china clays, except that they often contain a higher proportion of alkalis and iron. They are more vitreous when fired and do not burn so white as the china clays. A commercial sample of ball clay loses about 6 to 10 percent of weight when 'bone dry,'

and 15 to 20 percent more when fired to a red heat. Ball clays generally contain 3 to 4 percent of carbon as lignite or other organic matter of vegetable origin but they are seldom reported in the analyses as such.

Bentonite. This is a peculiar type of clay, considered to be the disintegration product of the glassy particles of volcanic ash or tuff. It always occurs in bedded deposits of varying depth and often inter-stratified with sand, clay or shale.

Bentonite is widely distributed in the United States of America and many other countries and used mainly for the following purposes :—

As a suspending agent for pottery glazes and enamels. For dewatering and clarifying petroleum and other oils. As a mordant in the dye industry and as a base for the lake colours, as a bond for sand in foundry work. As a substitute for plastic clay in the ceramic, pencil and crayon industries, and in some pharmaceutical and cosmetic preparations.

In chemical composition bentonites contain more silica, lime and magnesia than the ball clays but the alumina content is much lower. The iron content varies widely but is generally much higher than that of ball clays or kaolins.

The colour of bentonite varies greatly. Pale cream to buff are common colours but grey, pink or yellow colours are also found.

The texture is often compressed and hard but some specimens are found open and porous.

On soaking with water bentonites swell and crumble. Some contain a large amount of very fine material which remain in permanent suspension in water.

Two typical analyses of bentonite are given below. No. 1 is a washed sample of pink variety while No. 2 is an unwashed crude sample.

	1	2
SiO ₂	51.56	50.33
TiO ₂	.78
Al ₂ O ₃	13.42	16.42
Fe ₂ O ₃	3.22	2.42
CaO	2.04	1.39
MgO	4.94	4.10
K ₂ O	.38	1.00
Na ₂ O	.24	.12
H ₂ O	23.46	23.95
Total.	<u>100.04</u>	<u>99.73.</u>

(3) *Fusible clays.* Fusible clays generally fuse and lose their shape at relatively low temperatures. Some of these clays do not melt completely below porcelain heat and are useful in making common pottery and tiles, whereas the most common varieties are used for making common bricks. These clays generally contain rather a large proportion of silica, mostly in free state and also fluxes, like lime, soda and potash. These substances combine at a dull red heat, forming fusible silicates which melt down when heated to a higher temperature.

Colour of these fusible clays are very variable, the fired body being red or orange to yellow, or brownish

or greenish-yellow, according to the proportion of iron compounds and other materials, such as lime and magnesia present in the clays. Many clays will produce good wares if burned to just the right temperature, upon the possibilities of which depends the commercial value of the clay. Uniformity of size and satisfactory colour range are essential features for producing good quality wares out of common clays.

Shales are naturally indurated clays which have been compressed hard under the pressure of the superimposed mass or strata. They generally occur in stratified layers, and occupy an intermediate position between clay and slate. Shales vary greatly in composition and are used accordingly for various purposes.

Loams. Loams are composed of clay, sand and vegetable moulds and are generally used for tiles and bricks.

Loess. These are impure silty clays often calcareous and commonly a water deposit but may at times have been formed by the wind action. Loess are very common throughout the Mississippi valley and much used for common brick making. The colour varies from yellow to brown. The silt deposits of the Gangetic valley belong to this class and used for the same purpose.

Impurities in clays. When regarded as an impurity in clay, silica may be present in the following forms : (a) Hydrated silica, (b) uncombined or free silica e. g. quartz, sandstone, flint etc., and (c) silicates or combined silica such as felspar, mica etc.

Hydrated silica usually occurs in the form of a colloidal gel and may probably be considered as colloidal silica. It differs from many organic colloidal gels in possessing little plasticity, so it does not materially enhance the plasticity of the clay.

Uncombined silica occurs in clays mostly as amorphous silica such as flint, chert, chalcedony etc., or as crystalline silica such as quartz, sand etc. The former does not occur in good clays. Sand is a term used to indicate small grains of silica in the form of quartz, quartzite, or of other minerals of high siliceous character.

Sand is valued in ceramic industry according to the percentage of silica it contains. The purest sand consists almost wholly of silica but there are sands which contain only 40 per cent of this oxide. Felspathic or micaceous sands introduce alkalis into the body and may seriously alter the properties of the fired goods, causing them to vitrify at lower temperatures or even to lose their shapes before the firing is complete. When pure sand is not available, one containing grains of felspar is preferred to sands containing mica dust, as the latter being very thin are more easily affected by heat although mica softens at higher temperature than felspar. Addition of silica to the purest clays reduces their refractoriness through the combination of free silica with the alumina and forming silica-alumina eutectic. Seger in 1880 showed that the eutectic mixture forms with a ratio of 90 per cent SiO_2 and 10 per cent Al_2O_3 and melts at about 1650°C . According

to Bowen and Greig (1924) the eutectic composition of the silica-alumina system is 94.5 per cent silica and 5.5 per cent alumina melting at 1545°C. On rapid cooling, the melt turns into a simple glass with traces of mullite crystals but when cooled under equilibrium conditions it consists of a mixture of mullite and cristobalite.

Briefly speaking, the effects of the presence of silica in plastic clays are, to reduce its plasticity, shrinkage, the tendency to warp and crack and also the tensile and crushing strength of the body. On the other hand it increases the porosity of the body after firing and also the power to withstand sudden changes of temperatures.

Alkalies, in clays may be present either as soluble salts or as insoluble compounds. The effects of alkalies present in clays may be summed up as follows: (a) to increase the fusibility, (b) to produce a scum on the surface of the goods either on drying or after firing, and (c) to diminish the plasticity of the clay when it is made up into a slip with water and so to facilitate casting. The most usual form of alkalies present in clays are the alkali-alumino-silicates such as feldspar, mica, etc. Although the usual reports of analyses state the percentage of alkalies in terms of potash (K_2O) and soda (Na_2O), these oxides seldom exist in clays in these forms. The presence of a small amount of alkalies and ashes in a refractory clay may increase its strength by binding the particles together, producing a stronger mass. At the high temperatures reached in certain firing, a partial volatilisation of

alkalies takes place, the material then becoming more refractory.

The most common form of mica present in clays is muscovite or potash mica. It is a double silicate of potash and alumina and can be roughly represented as $K_2O.3Al_2O_3.6SiO_2$. Rieke found its fusion point corresponding to seger cone 13 (1395°C). The softening effect of mica on a refractory clay is seldom noticeable below 1200°C but when very finely divided its action begins at a much lower temperature.

Morey and Bowen (1925) have shown that the binary mixtures of sodium meta-silicate ($Na_2O.SiO_2$) and free silica (SiO_2) form several eutectic mixtures. 77 parts of $Na_2O.SiO_2$ and 23 parts of SiO_2 melt at 840°C whereas $Na_2O.SiO_2$ 53 and SiO_2 47 melt at 693°C. The melting temperature of $Na_2O.SiO_2$ is 1088°C.

Organic Compounds, when present in clays should not exceed 5 per cent as otherwise the clay is seldom workable. The chief effects of carbonaceous matter in a clay are, (a) its colour before and after firing, (b) increase of plasticity due to humus, (c) increase of porosity of the clay after firing, (d) increased amount of water absorbed in the green state and consequently greater amount of shrinkage, (e) smaller amount of fuel required to burn the clay specially when the carbonaceous matter like lignite create no difficulty in firing.

The most troublesome effect of the presence of organic matter in clays is their powerful reducing effect on the oxides of iron and great care is necessary to

burn off the carbon with a plentiful supply of air before the reduced iron can form a fused slag or core.

Lime and Magnesia, compounds generally occur in clays as carbonates or sulphates and their amounts vary to a large extent according to the nature of the clay. The reactions of lime and magnesia with clays are very complex and their nature is not clearly known.

The effect of lime on clay has been shown by Rieke. According to him 35 per cent of lime (CaO) lowers the fusion point of clay to cone 7 (1230°C) but the action of lime may be altered by the presence of other fluxes in the clay. When alkalies are present simultaneously with lime, they reduce the temperature at which the glassy material is formed, as silicates of potash and their aluminosilicates are formed, at a lower temperature than the corresponding lime compounds, and these fused matters act as solvent on the other materials.

According to Rankin and Wright (1915) several compounds are formed with the combination of lime and free silica. At about 1200°C the meta-silicate or wollastonite ($\text{CaO} \cdot \text{SiO}_2$) is observed. The $3\text{CaO} \cdot 2\text{SiO}_2$ compound is formed with the combination of 54.5 parts of CaO and 45.5 parts of SiO_2 which melts at 1455°C .

According to Rieke 45 per cent of magnesite (MgCO_3) in clay lowers its fusion point down to cone 10 (1300°C) but with greater proportions, however, the refractoriness increases.

Rankin and Merwin (1918) found that a ternary eutectic is formed at 1345°C between 20.3 parts MgO , 18.3 parts Al_2O_3 and 16.4 parts of SiO_2 . Ferguson and

Merwin (1919) produced an eutectic between CaO 30.6, MgO 8 and SiO_2 61.4 parts which melt at 1320°C .

Magnesia and magnesite increase the shrinkage of a clay and also make it extremely 'short,' but articles made from such mixtures, retain their shape in a remarkable manner when fired. In the case of lime or chalk mixtures, the range of vitrification is very short and consequently articles made of such mixtures get overfired very easily. It appears that the molten magnesia complex is very viscous and tacky whilst similar lime complex is a very thin and mobile fluid which readily attacks the surrounding particles.

A marked feature of lime in clay is the colour produced after firing. A clay containing sufficient iron to burn red, will, when impregnated with lime, burn to buff, changing at higher temperature to yellow-green and finally to a decided green, provided the atmosphere of the kiln is sufficiently reducing. The red colour due to iron generally disappears when the latter begins to combine with the lime and silica to form a lime-iron-silicate. The final green colour is due to the full development of the latter compound which is so prominent in common glass. Iron does not enter into chemical combination with lime in the ferric state, so that in a continuous kiln where the atmosphere is mostly oxidising, the products are generally red streaked with buff or vice versa.

Iron compounds, are invariably present in all natural clays and even the most careful attempts at purification do not succeed in removing all the iron present in the

clay. The chief compounds of iron generally present in clays are the two oxides (more or less hydrated), carbonates and sulphides.

Sosman and Merwin (1916) found that an eutectic between lime and iron oxides which melts at 1203°C has the composition of 8 per cent CaO and 92 per cent Fe_2O_3 .

The red colour of certain clay product is apparently due to the presence of iron oxides but no attempt has been quite successful to produce the same shade on white burning clays by the addition of theoretical amounts of artificial oxides. The colour thus obtained is generally brownish red but far less deep and less brilliant, than that of a natural clay.

Ferrous oxide (FeO) occurs but very rarely in clays though it is some times produced in the kiln by the reducing actions of the fire gases or the carbon present in the clay. It readily unites with silica in clay to form a dark slag-like compound. The most fusible mixture of this oxide and clay has according to Rieke the formula- $2\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and this eutectic mixture is formed with 39 per cent of the said oxide with 61 parts of clay fusing at 1140°C . FeO produces more fluidity than MgO .

Both carbonates and sulphides, when heated to a temperature above 1000°C , decompose, leaving ferrous oxide with evolution of gases, which are detrimental to the burnt products. If however, the atmosphere of the kiln is sufficiently oxidising, the unstable ferrous oxide is turned into red ferric oxide which is very refractory

and does not do much harm to the products. It is therefore of great importance that, between 700°C and 900°C , the atmosphere inside the kiln should be strongly oxidising and as free as possible from CO_2 and SO_2 gases. In reducing atmosphere ferrous oxide imparts a light blue tint when in small proportion, but as the proportion of the oxide increases, the colour deepens rapidly and passes to black with a metallic reflection.

Titanium. is mostly present in clays as rutile (TiO_2) or titanite (CaTiO_3) and they act as somewhat powerful fluxes. Clays which are required to be highly refractory should not contain more than 2 per cent of this oxide. Ten per cent of TiO_2 lowers the softening point of kaolin by about 100°C .

Plasticity. plasticity of clays can be defined as the property which enables them to change their shape without cracking, when they are subjected to a deforming stress. In other words, a material is said to be plastic when it can be kneaded or pressed into a desired shape, and it remains in that shape when the pressure is removed.

According to this general definition most metals are plastic solids which require higher pressures to start the flow or deformation of shape. Clays develop their plasticity only when water is added to them. Each clay requires a definite amount of water to develop its maximum plasticity. If more water is added the clay becomes sticky and with less water it is too short for proper working at the ordinary pressure. This water content necessary to develop the maximum plasticity of clay is known as

water of plasticity and depends on the nature of the clay and the pressure applied during formation. When pressure is increased to give the form of a clayey body this water of plasticity required will be less. J. W. Mellor (1922) found that increasing the pressure from 1 to 200 kilograms per sq. centimeter, the water content for an earthenware body was reduced from 26.4 to 5.6 per cent. This water content increases with the increase of plasticity of a clay.

Several attempts have been made from time to time to explain the cause of plasticity in clays but none of them is wholly satisfactory. The various theories proposed are as follows :—

- (a) The size and shape of the solid particles.
- (b) The aggregation of the particles.
- (c) The inter-molecular attraction between the solid and liquid.
- (d) The presence of soluble salts and organic substances.
- (e) The effect of water on the solid particles and colloidal phenomena connected therewith.

Wheeler (1896) found that quartz and limestones when ground sufficiently fine to pass through a 200 mesh sieve show a little plasticity but do not hold together when dried. According to Le Chatelier and others, mica and glauconite, if ground very fine, produce a paste equally as plastic as clay, due to their laminar nature.

It has been shown that both extremely fine grained, as also coarse grained clays are less plastic than clays containing mixed grains. B. Zschokke (1903) and F. F. Grout (1905) have shown that the plasticity of some clays is lessened by finer grinding. Mellor suggested (1921) that a distribution of grains of various sizes which permit the closest possible packing, gives the maximum plasticity,

The hydration theory of plasticity is explained by the attraction between the solid clay particles and the film of water surrounding them. The plasticity of clay can increase with the increasing proportion of water so long as the average thickness of the surface film on the particles of clay is not greater than the average range of the molecular attraction of the clay for water. When this water film is thicker, part of the water will be outside the range of this attraction and the clay will be less coherent and become sticky.

The soluble salt theory was advanced by Purdy and Moore in 1907 but Seger had several times noted that there seemed to be a close relationship between the amount of soluble salts present in a clay and its plasticity. He observed that bricks made from very plastic clays are peculiarly liable to efflorescence due to soluble salts coming out on the surface. According to this theory, the absorbed or otherwise held salts, form on addition of water, a viscous solution round the grains of clay enveloping them with a liquid of high tension. The fact that flint and other like minerals of surface factor equal to that of clay do not develop

plasticity when soluble salts are added to them, is accounted for by saying that clay particles have an absorptive power far in excess of that of any other mineral.

Geller and Caldwell (1921) have shown that Florida kaolins can absorb up to 0.25 per cent of NaOH completely. Asley has used this absorptive power of clays to determine the plasticity thereof.

P. Rohland (1902) regarded plastic clays as consisting of very fine amorphous nonplastic grains or cores surrounded by films of materials in the colloidal gel state. When maximum plasticity is developed this film becomes saturated with water. When the clay is dry, the colloidal matters become hard and their gelatinous property is lost, so that the solid particles cannot move over one another with the same facility as in the moist condition. If on the other hand an excess of water is added, the solid particles are in suspension in the surrounding material and produce a clay slip. He further suggested that the plasticity of a clay depends on the amount of hydrolysis which the materials have undergone, so that a kaoline which is scarcely hydrolysed, has very little plasticity, while a very plastic ball clay appears to have been highly hydrolysed. The amount of hydrolysis which can occur in a clay, depends chiefly on the presence of free alkalis, a sufficiently high temperature and a very prolonged period of action. Mellor found that if ground pitcher, felspar or cornish stone, is heated with water under pressure, at a temperature of 300°C for several

days, a gelatinous coating is produced on their grains which render them feebly plastic. This action however is not evident in the absence of alkalies.

According to G.A. Bole (1922) the plasticity in clays is caused by the adsorbed film of colloidal materials surrounding the grains of clay, which are negatively charged, the film being of opposite polarity. When a strong electrolyte is added having the same polarity as that of the clay particles the film will be attracted by the stronger ions and leave the clay particles. The clay particles which were in mutual contact through their adsorbed colloidal film will now repel each other, due to their increased like polarity. The viscosity of the clay slip will decrease resulting in a more fluidity of the mass. When an electrolyte of the same polarity as the colloidal film is added, it will drive the colloidal particles toward the clay particles causing an increase in the depth of the colloidal film surrounding the clay particles. The maximum plasticity of a given clay is developed when the colloidal films are the thickest.

Measurement of plasticity. The problem of measuring the plasticity of clays has not been very satisfactorily solved. Many methods have been suggested from time to time but objections have been raised against most of them.

The most common practice still used consists in judging the plasticity by feel and grading the clay as *fat* or highly plastic and *lean* or low plastic. An experienced hand can do the job quite satisfactorily.

For measuring plasticity by mechanical method Bischof suggested to force the plastic clay through a nozzle of a wide cylinder till the pencil so formed breaks of its own weight. The longer the length of this pencil the more plastic the clay is.

Langenbeck and Grout advocated the use of Vicat's needle, to find the maximum plasticity developed by a clay. Grout (1905) measured the strength by the weight required to force a Vicat's needle of 7 sq. c.m. cross section to a depth of 4 c.m. in half a minute.

Zschokke (1904) prepared test cylinders 60 m. m. high and 30 m.m. in diameter and subjected the freshly prepared cylinders under a stretching machine till they broke into two. He multiplied the percentage of this deformity with the tensile strength of the test piece and the product he termed as *plasticity co-efficient*. The objection raised against this method is that the degree of extensibility of the test piece depends on the rate of stretching force. A rapid rate of stretching gives higher figure.

Asley (1911) found the absorptive power of colloids present in clays by using solutions of malachite green (6 grams per litre) and suggested that the colloid content of a clay is the indication of its plasticity. It has been pointed out by critics specially Mellor (1922) that colloids present in clays are of different natures and have different powers of absorption. The dark ball clays contain large quantities of organic colloids which must differ from the colloids present in primary

kaolins. The soluble salts present in clays must have some effect on the colouring matter.

Atterberg (1911) proposed a *plasticity number* based on the assumption that plasticity of clays varies as the range in water content of the workable clay, the fat clays possessing a greater range.

Atterberg classifies the condition of a clay with varying amounts of water into five states, as follows : (1) the upper limit of fluidity or the point where the clay slip flows as water ; (2) the lower limit of fluidity or flow where two portions of the clay mass can be made barely to flow together when placed in a shallow dish, which is sharply rapped with the hand; (3) the normal consistency, or the condition in which the clay is most workable, is no longer sticky and will not adhere to metal; (4) the rolling limit, or the condition in which the clay can no longer be rolled into so-called threads between the hand and the surface on which it may rest. This is the lower limit of the workable condition; (5) the condition in which the damp clay will no longer hold together when subjected to pressure.

The water contents of the conditions 2 and 4 are determined and the difference between these two amounts is expressed as the *plasticity number* of the clay.

To determine these water contents 5 grams of the clay powdered to 120 mesh are put into a small porcelain evaporating dish and water added to form a paste. The mass is then spread out in a layer 1 cm. thick,

a triangular groove is cut through the paste, and the dish tapped sharply against the hand. Clay is then added until the mass is so stiff that it will barely flow together. The water content is then determined. To determine the rolling limit the clay in a stiff condition is rolled on paper to form threads. Clay is then added until the threads crumble, when another water determination is made. This gives the rolling limit.

In this method too much personal factor is involved and the same clay produces different numbers when worked by different persons.

In Sringer and Emery method as described by Mellor (1922) a spherical ball of plastic clay, 2 centimeters in diameter, is placed on a glass plate beneath a piston of which the vertical movements can be measured. Sufficient fine shot is allowed to flow into a bucket at the top of the piston to cause it to descend and deform the sphere until it cracks.

Now if P denotes the plasticity of the wet clay, R the pressure the clay has resisted and S the amount of deformation suffered without cracking, then, with A and B as constant,

$$P=K (R+A) (S+B)$$

By a suitable choice of units or regarding the apparatus as standard for comparison the constants can be cut out so that the plasticity may be regarded as the product of the pressure and the deformation.

Hall has objected to this method as it is difficult to obtain concordant results.

Talwalker and Permelee (1927) devised a new apparatus to determine the stress-strain relations of different clays with varying percentages of water content. They say that there is a certain limit for all clays tested, to which the strain is proportional to stress, but beyond this point, which is called the proportional limit, the deformation rate is much higher. A definition of plasticity according to these workers is given in what they called *plasticity index* expressed thus :—

$$\text{Plasticity Index} = \frac{\text{Total deformation at the point of failure.}}{\text{Average stress beyond proportional limit.}}$$

Whittemore (1935) presented a method of measuring the plasticity of clays and mixtures of clays, by using an apparatus by which the penetration of a constantly loaded hemisphere into a plastic clay mass during a definite time period is measured. With his data he established a formula :— $d = atp$, where d = amount of penetration during a time period t , a is related to the load used, the diameter of the hemisphere, and some of the properties of the clays, p in the formula is the measure of the plastic properties of the clay. The use of a hemispherical plunger avoided the errors generally observed from a flat ended shaft when false results would be obtained in testing clays containing large grains that are so located at the end of the shaft that

part of the grain would extend beyond the circumference of the shaft. The protruding grains would actually increase the area of the clay acted upon by the deforming load and give results that could not be compared with results on the same clay when ground finer.

Effect of electrolytes on clays. As already stated, clays are weathering products of rocks from which the most soluble portions have been removed. By the prolonged action of water on this residual product some portions of the insoluble matter has been converted into the *colloidal state*, that is, the particles have been converted into such a fine state that they will remain suspended in water for a pretty long time without settling down like other coarser particles. The amount of this colloidal matter in a particular deposit of clay depends mainly on its past history and the length of time that the clay is exposed to the action of water. The old method of washing china clay in England where the clay slip is carried for miles through channels, produces decidedly more plastic clays than the quick German method. The ball clays which were exposed to prolonged actions of water contain more colloidal substance than the china clays. Colloids present in clays may be either of organic or of inorganic origin. A colloidal solution can be detected from a true solution or crystalloid by passing a strong beam of light through the liquid when the former will appear turbid while the latter is absolutely clear. They can be separated by ultra filtration through collodion, gelatine or animal membranes.

When a small amount of acids, acid salts of metals or common salt is added to a colloidal solution, the fine particles will coagulate together and settle down forming a colloidal gel. This change is termed as *flocculation* or *agglomeration* of the colloids. The reverse change takes place when very small amount of chemicals like ammonia, or the hydroxides, carbonates, silicates and borates of alkalies are added to a colloidal gel. This change from a gel to a solution or sol form is called *deflocculation* or *peptization*. The chemicals used for these purposes are termed as *electrolytes*.

Salts which dissociate into acid and basic ions may cause either flocculation or deflocculation. Ammonium chloride, magnesium sulphate and borax when used as electrolyte in enamel slip flocculate the same and help in the setting.

When a clay is suspended in pure water it does not give any reaction with the common indicators but when a very small amount of alkali is added, it increases the dispersion of the clay particles and reduces the viscosity of the clay water suspension. This is explained by the theory that the negatively charged clay particles are repelled by the similar charge of the OH' ions which increases the dispersion of the system or causes deflocculations of the clay particles. This dispersion increases until a certain concentration of the alkali or OH' ions is reached when further addition of the alkali will decrease the dispersion. In other word, the clay will begin to flocculate. Hall (1923)

has found that the point of maximum deflocculation varies for different clays between pH 11 and pH 12.

When a clay slip for casting is required to be stored for some time, it has been found in practice that the slip has a tendency to flocculate when it contains just enough alkali to bring to the state of maximum deflocculation but if the slip contains an excess of alkali the thickening may not occur. This effect is explained by the facts that a portion of the alkali is absorbed by the clay particles which may get disintegrated to further subdivisions by the continued actions of water and salts. A portion of the electrolyte may also be used up by the chemical reactions with the soluble salts present in the clay specially the sulphates.

When acids or acid salts of metals are added to a clay slip a reverse action takes place. The fine clay particles coagulate together enclosing a large amount of water between them which increases the viscosity and the plasticity of the clay. The clay particles begin to settle down quickly until a certain point is reached. Hall found that the rate of maximum settling of several clays varies between pH 2.7 and pH 4. This wide range is due to the diverse nature of the different types of colloids present in clays. This increase of plasticity due to the addition of acids is made use of to increase the workability of lean clay bodies specially in the porcelain industry.

Protective colloids. Substances like gelatine, gums, tannin or dextrine when added in a clay suspension

are easily dispersed by the water and the clay particles get coated with these colloidal substances so that there is no further action of any acid or acid salt on the clayey colloids. Hence these substances are known as protective colloids. A protective colloid may not be able to deflocculate a clay slip itself but it prevents the flocculation and settling down of the slip by another substance of acid nature. Clay slips, which coagulate with long standing, will not do so when tannic or gallic acids are used as protective agents.

These phenomena of colloids are made use of in the purification of clays and in making clay slip for casting. For the latter purpose a clay slip is made thinner with the addition of small amounts of electrolytes so that a properly adjusted clay slip contains less water than a stiff mud of clay without electrolyte. The nature and amount of electrolytes for a particular clay has to be determined by actual experiment. The presence of soluble salts in a clay interfere in making a casting slip with it.

Determination of Electrolyte. In order to make an easily flowing casting slip from a clay or clayey mixture it is essential to carry out experiments to determine the nature and exact amount of electrolytes which give the maximum flow of the clay slip. The rate of the flow depends on the change of viscosity in the clay. There are various methods and apparatus suggested to determine the viscosity of clay slip. The most simple and easily available apparatus for the purpose is described below.

A glass tube one foot long and 1.5 inches wide is provided with corks at both ends. The upper cork is provided with a narrow glass tube of $\frac{1}{4}$ inch bore while the lower cork is provided with a similar tube having a piece of rubber tube and a pinch cock attached to its lower end.

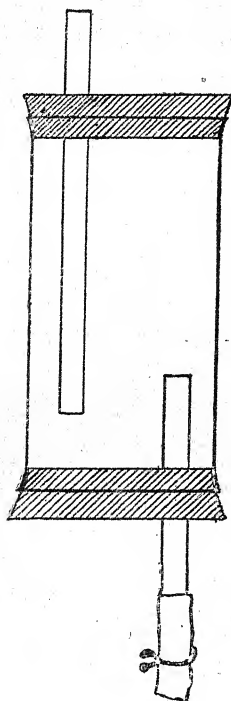


Fig. 6 A simple Viscosimeter.

The clay for testing is first converted into a thick slip with about 60 per cent water. A very small

amount of an electrolyte, (0.05 per cent) is then added into the clay slip and thoroughly mixed for sometime when it will be noted that the slip becomes thinner. The slip is filled into the viscosimeter and allowed to flow down the lower tube; the time of flow between two marks on the side of the wide tube being noted. The experiment is repeated with further addition of electrolyte till the time of flow of a given amount of slip is minimum. This point gives the maximum of electrolyte required for the particular clay to produce the minimum viscosity. The upper narrow tube serves to stir up the clay slip by drawing air bubbles through it.

The specific differences of carbonate and silicate of soda as deflocculants are studied and reported by several workers from time to time. For the general bulk of earthenware and porcelain bodies sodium silicate produces a greater fluidity and at a lower Na_2O content than sodium carbonate. If the silicate contains high silica ratio the slip gets flocculated again rather quickly. Webb (1934) is of opinion that the silicates producing maximum fluidity have compositions between.

Na_2O . 2.3 to 2.5 SiO_2 .

Ageing and Souring. Ageing and souring are terms applied to the process of storing clay in a damp cool place in order to increase its plasticity. The reactions that take place are probably the decomposition of organic matters present in the clay with the formation of dilute acids which coagulate the fine grains of clay and thus tend to increase the plasticity. The presence

of an excess amount of free alkali in the clay may limit or even prevent improvement by ageing. In such cases Seger suggested the addition of a little amount of old vinegar or acetic acid to improve the action of souring.

Rohland stipulated that souring should take place in a cool atmosphere, as it is fundamentally a colloidal phenomenon, whereas H. Spurrier and A. S. Watts are of opinion that when souring or ageing a clay, a temperature between 80° to 90° F is preferable. It is the opinion of old English potters that china clay which is dried by slow heat on a 'dry pan' seems to be more plastic than the clay which is filter-pressed and dried rapidly in tunnel driers or such other devices.

Recent experiments by Glick and Baker have shown that bacteria play an important part in the development of plasticity in clays on ageing. A clay mixture originally containing a considerable variety of bacteria, on ageing for a few months was found to contain a reduced number of species but an increased number of living bacteria and an absence of moulds and yeast. The best temperature for developing the living organisms according to these investigators was 85°F and it was found that up to one month the plastic property is improved almost proportionately.

The plasticity of a clay may be increased by the addition of colloidal gels, alumina, hot starch, dextrin, gelatin, glycogen or other enzymes and by tannin. This sort of artificial plasticity or pseudo-plasticity is

quite different from natural plasticity which can be augmented a little by grinding and pugging the body with water for a long time in order to increase the hydrolysis in the clay materials.

Weathering. In this process the clay is subjected to the actions of the atmospheric agents, the sun, rain, frost, snow and the wind. The alternate heating and cooling of the clay particles break them down into finer grains which get hydrolysed by the prolonged action of water forming more colloidal substance and increase the plasticity of a clay. Weathering also reduces the impurities in a clay. The insoluble iron salts present in the clay are rendered soluble by the actions of air and water and a shower of rain will leach out the soluble salts and make the clay more refractory and homogeneous. A comparative study of a fire clay before and after weathering will convince the effect of weathering.

Before weathering.		After weathering.
SiO ₂	... 64.62	64.7
Al ₂ O ₃	... 21.65	22.9
Fe ₂ O ₃	... 1.48	1.3
CaO	... 1.98	1.0
Alkalies...	1.62	0.7
Loss	... 8.52	9.5
	<hr/> 99.87	<hr/> 100.1

In cases where the impurities are not reduced to appreciable extent, their injurious effect, is much

diminished by the process of weathering. The iron and other impurities in such cases are very finely divided and uniformly distributed throughout the mass of the clay and on firing, the presence of these impurities do not do any harm.

Felspar. Felspar is a class name for a group of related minerals and they are the most important constituents of rocks. Nearly 60 per cent of the materials contained in the igneous rocks are felspars. In Germany this mineral is generally termed as feldspar and the commonly accepted formula for them is $RO \cdot Al_2O_3 \cdot 6SiO_2$ where RO stands for the basic oxides such as potash, soda or lime. In round number a good potash felspar possesses the composition :—

SiO_2 65, Al_2O_3 18 and K_2O 16·5 per cent.

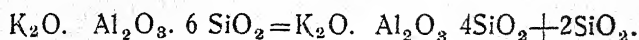
The iron oxide content must not exceed 0·5 per cent for making white body.

The different kinds of felspar cannot be sharply distinguished from one another; they pass gradually from one to the other variety. Thus, the soda felspars or *Albite* pass to the potash one or *orthoclase* by the simple substitution of potash for soda. The specific gravity of this series varies from 2·5 to 2·6, the lower value generally is for the orthoclase variety. Orthoclase is the chief variety largely used in pottery manufacture.

The pure alkali felspars are transparent and colourless. The colour of many felspars are due to the presence of various microscopic inclusions which act

as pigments. The opacity of some felspar crystals may arise from a multitude of colourless inclusions. The yellowish, pink or red tints may come from oxides of iron although after calcination the red Scandinavian felspars often have a whiter colour than the white Canadian variety. The pinkish felspars are usually potash ones although some soda felspars have the same tint. Dark grey felspars are common in the lime variety or *anorthite*.

Orthoclase has no sharp melting point. It softens slowly with the rise of temperature and when finely powdered it softens more easily and at comparatively lower temperatures. The reported fusion temperatures of felspars range from 1130°C to 1200°C. Felspar expands slightly when calcined at 1170°C and the specific gravity is also reduced a little, due to the inversion of orthoclase into *lucite*,



The fused felspar exhibits a milky white aspect.

Powdered albite moistened with water turns red litmus blue. The water hydrolises the mineral and produces alkali silicate. When orthoclase is finely ground in water, a certain amount of potassium is dissolved in water and the amount dissolved is increased by the addition of such substances as ammonium salts, lime and gypsum. Felspars are highly susceptible to natural influences and the most common end products of the reactions are quartz and kaolin, but other hydrated aluminium silicates are also formed.

According to Seger, feldspars possess basic properties in the porcelain fire and show a supersaturation with alkalis at this temperature. If no quartz is present in the body, this alkali acts on the clay, producing no vitreous mass nor lustre, but if quartz is present, it acts on the alkali and the vitreous and glossy appearance characteristic of porcelain arises.

A few analyses of orthoclase feldspars are given below.

Variety	Silica	Alumina	Iron	Lime	Magnesia	Alkalies	Loss
1. Norwegion	64.70	20.22	0.08	trace	nil	14.78	0.78
2. Swedish	65.85	19.32	0.24	0.56	0.08	14.10	0.8
3. German (Bayern)	64.10	21.46	0.34	0.44	0.12	13.05	0.66
4. Indian							
(a) Alwar	68.96	18.26	0.18	0.55	0.5	11.58	0.5
(b) Ajmere	64.2	21.33	0.05	0.14	0.06	13.61	0.6
(c) Bangalore (Arjunabeth)	65.61	18	68	0.29	trace	16.12	0.08
(d) Ramgarh.	65.44	19.84	0.03	0.85	0.14	13.85	0.3
(e) Gaya (Gurpa)	63.83	21.11	0.08	0.21	0.07	13.25	0.28

China stones are partially decomposed granite rocks and are generally composed of quartz and felspar, fresh and partially kaolinised. In chemical composition they resemble the rock pegmatite and are used as substitutes for felspar. This material is largely in use in England, specially a local variety found in abundance in Cornwall and known as *Cornish stone*. It is a pale granitic rock of medium coarseness and exhibits kaolinisation of the felspar sufficiently to give a rather powdery aspect to the fracture. There is no sharp demarcation between the china-stone and the partly kaolinised china-clay rock. In some cases both of them are worked side by side in the same excavation.

China-stone is too hard to be broken down like the china-clay rock; it must be blasted and quarried in the same way as ordinary granite.

There are several varieties of china stones, but the one greatly in demand by the potters is called hard purple, with a faint purple tinge caused by the presence of purple fluorspar.

These stones are ground wet in huge wooden pans paved with chert stones. The 'runner', a big block of chert, drives the stones and causes them to grind against each other till the stones are very finely powdered, and made into slurry in which state it is generally sold to the potters. The wet ground china stones are slightly more plastic than similarly ground felspars.

The specific gravity of china-stone is about 2.6 and it fuses at about 1200°C to a glassy mass.

A few analyses of China-stones are given below.

Variety	Silica	Alumina	Iron	Lime	Magnesia	Alkalies	Loss
1. English. (Hardpurple)	70.31	16.75	1.50	1.30	0.08	7.31	2.58
2. American (Texas)	68.88	16.77	0.83	0.99	0.17	6.77	5.79
3. French (Limoges)	76.11	14.61	0.66	1.44	0.42	6.02	1.23
4. Chinese (Pe-tun-tse)	75.90	13.90	0.70	0.40	trace	5.17	2.7
5. German (Pegmatite)	82.49	11.05	0.41	0.05	trace	4.17	1.88

Quartz and flints. These are different forms of silica found in nature in abundance. The different forms of silica can be arranged in three main groups. The crystalline group contains the three forms of crystalline silica—quartz, tridymite and cristobalite, which are quite different from each other in their physical properties but have the same chemical composition— SiO_2 . When pure, quartz is quite colourless, used for optical purposes and is known as *crystal*. But it is seldom found perfectly pure, usually containing a small proportion of impurity, which may colour the crystals or cause them to become cloudy or opaque. It has a specific gravity of about 2.65.

When heated to about 870°C quartz crystal changes to a different form known as *tridymite* with an expansion in volume of about 16 per cent and lowering of the

sp. gr to about 2.27. On further heating to about 1470°C the sp. gr increases to about 2.34 attended by a slight contraction of about 2 per cent, and this form is known as *Crystobalite*. When the mass is again heated to 1685°C, the *crystobalite* melts to a silica glass with a sp. gr of 2.21 and an expansion in volume to about 20 per cent. The molecular motion within these different phases is very slow and two phases can often be kept together at the ordinary temperature for a long time although the tendency is to change for the stable form.

The opals, or the non-crystalline hydrated silica contain upto 12 per cent water. Selected specimens are much admired as gem stones for they are said to reflect all the prismatic colours in refulgent tints of indescribable brilliance.

Flint, chert, chalcedony, contain more or less amorphous silica, associated with minute crystalline silica so difficult to recognise that these minerals were once thought to be amorphous silica, but now they are recognised to be in the crypto crystalline form. Flint occurs in nature as nodules or lumps of a grey or black colour. They are supposed to be formed by the slow precipitation of silica around a nucleus, consisting of a minute shell-fish, sponge, or other organism. They usually contain about 95 per cent of silica, the chief impurities being chalk and organic matters. Flint has a specific gravity of about 2.6 and appears to melt at about 1750°C. It expands more than quartz on heating with lowering of specific gravity.

Calcined flint used in pottery has a specific gravity ranging between 2.3 to 2.4. Grey flints shatter more than the black ones during calcination on account of their faster rate of expansion. The colouring matters in flints appear to be nitrogenous hydrocarbons easily decomposable by heat.

The effects of calcining quartz and flint in a china biscuit oven (1300°C) are quite different; the one expands much quicker than the other and the density of the mass falls down accordingly. The change is very rapid with flint; with quartz it is relatively slow. A three-hour heating at Seger cone 35, converts about 65 per cent of the quartz into the less dense form, whereas three hours firing at a temperature as low as cone 14 will convert nearly all the flints from the dense to the less dense form. Not only the rate of expansion of flint during calcination is much faster than that of quartz but the fall of specific gravity of the former is much lower than that of the latter. Rieke and Endall (1913) have shown that the fall in the sp. gr of flint after one firing in a hard porcelain oven is to 2.23 while that of quartz sand is to 2.33 after ten firings in the same oven. Hence, it is not to be expected that calcined quartz and flint would behave similarly in pottery bodies.

The activity of the hard fired flint is very much greater than that of the less fired ones. Bodies made with uncalcined flint or quartz are more difficult to glaze, than bodies made with well calcined flint or quartz provided other things remain the same. The

uncalcined silica combines less readily with other materials and troubles may arise if the firing is not hard. The continental potters use a good deal of uncalcined sand and it is a custom with them to fire their wares to much higher temperatures than their English co-workers who use calcined flint.

The method of grinding has some influence on the ground mass. Dry ground flint contains smaller amount of very fine particles than wet ground flint. The influence of fineness of both flint and quartz has a far reaching effect on pottery bodies. Fine grinding of silica exerts more influence than fineness of spar in lowering the firing temperature. Increase of fineness of flint or quartz also amounts to the increase of the quantity of the same. Moreover, the finer the grains of silica in the body, the less is the porosity and crazing, and the more is the 'dunting' of the wares on fire

Bone Ash. This is prepared by calcining animal bones mainly of oxen. Those of horses or pigs are not used in pottery bodies as they give colouration to the fired articles. In chemical composition bone ash is calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ and it is largely used in making bone china.

The bones are first cleaned by boiling in water, then calcined carefully. Fully calcined bones are devoid of all plasticity when finely powdered and mixed with water and they are not so suitable in body mixture for this reason. Properly calcined bones generally contain one to two per cent of carbon left in them and the colour after calcination

is light grey and not clear white like fully calcined bones.

Plaster of Paris. When gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is heated to about 120°C , it loses the equivalent of $1\frac{1}{2}$ molecules of water, and forms a hemihydrate— $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$, a soft white powder called plaster of Paris, because of the large deposits of gypsum near Paris. This plaster sets into a hard mass when mixed with water. If gypsum is heated above 200°C , it passes into anhydrous calcium sulphate which does not harden or set and is called 'dead burnt' plaster. Admixtures of borax or alum retard the rate of setting of plaster while common salt accelerates it. Alum makes 'set' plaster much harder.

The amount of water added to the dry plaster to make it into a plastic mass, has got great influence on the 'set' plaster. The density, porosity and strength, all vary with the variation of this added water and this fact has to be considered when using plaster for different purposes. Plaster of Paris is a valuable material for making exact reproductions of statues, ornaments, decorative works and moulds etc. The slight expansion which occurs during the setting of plaster enables it to make a sharp reproduction of the details of the mould.

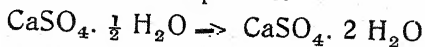
The right variety of gypsum used for making plaster of Paris is a white stone similar to marble but soft enough to be scratched easily by a knife. But before the stone is properly hydrated and fit for making plaster, it is darker in colour and harder in texture. This hard stone is generally used in the cement works.

Big blocks of gypsum stones are first air dried and then broken in jaw crusher into small pieces of about 2 inches in diameter. They are then spread on iron trays in single layers and the trays are placed in trolleys. The stones at this stage generally contain 23 to 25 per cent of water. The trolleys are now pushed into a small muffled tunnel oven heated with coal from outside up to a temperature of 180-190° C. The trolleys are kept in the oven for about 48 hours. Samples are drawn periodically from different trolleys and the amount of moisture content of the stones determined; when the average moisture in the calcined stones is about 6 per cent the trolleys are withdrawn from the oven.

Calcined gypsum becomes very soft and is pulverised between two vertical grinding stones, revolving on each side of a fixed stone, having grooves for pouring the small pieces of gypsum between them. The powder from this pulveriser is passed through an electromagnet and then pulverised again upto the required fineness. A well powdered plaster should leave no residue on a 90's sieve. When required in small quantity, gypsum is first powdered, sieved and then roasted in an iron pan on open fire with occasional stirring to calcine the plaster uniformly. The powder boils rapidly as the combined water is given off and when this boiling nearly stops after about 45 minutes, the plaster is ready for use.

Every sample of prepared plaster should be tested to keep up the standard quality. Firstly, the heat developed due to the chemical combination of water should

be determined. This determination fairly controls the composition of calcined plaster.



(6.2 P.C. water) (20.9 P.C. water)

A cup of plaster is mixed with a cup of water for about 5 minutes and then a thermometer is inserted into the thick mass. Temperature rises about 10° to 15°C in well-made plasters. The amount of expansion during the setting of plaster is determined by putting an iron band with a moveable index round a test piece. As the plaster expands, the index moves along a fixed scale. Every batch of plaster when mixed with same amount of water should develop equal amount of heat with the same amount of expansion under similar conditions; when variations are observed, the cause must be looked for in the raw materials or in the process of calcination.

Gypsum is found in good quantity in the Punjab near Jhelum and also in Rajputana at Marwar, Bikanir and Jodhpur. A large gypsum deposit has also been found recently near Hardwar in U. P.

CHAPTER III.

FORMATION, DRYING AND FIRING OF WARES.

Treatment of raw materials. The materials used for making pottery wares, except the clays, are hard stony substances. These substances must be pulverised to fine powder before they can be mixed with the soft clays to form a mixture of mass which is technically known to the potters as *Body*. Hard minerals like quartz, felspar, marble etc are ground to fine powder in different stages. In the first stage the materials are crushed to small pieces of half inch to one inch in size in a powerful mill known as the *Jaw crusher*. This mill consists of a pair of corrugated hard steel plates known as the jaws placed in front of each other at an angle. The distance between the two jaws can be adjusted according to the size of the crushed material required. Big lumps of minerals are thrown between these two jaws which by their to and fro movements actuated by very powerful mechanism crush the hard minerals into small bits which fall below through the small space left between the two jaws. One such machine with a jaw opening space 6 by 12 inches will crush about 2 tons of material per hour, the size of the crushed pieces being about one inch.

The crushed materials are then ground further in a *pan roller mill* to sufficient fineness that they pass

through a sieve of 20 to 30 mesh. This mill as the name suggests consists of an iron pan with flat bottom which is paved with hard siliceous material, and a pair of rollers made of hard granite stone rotate over the pan on a horizontal axis. The material is crushed between the rollers and the stone paving of the pan and is automatically sieved through a coarse sieve attached to the base of the pan; a pair of brushes force the ground material over the sieve and then bring back the coarser particles to be ground again. When hard fire clays or shales are to be ground, both the pan base and the rollers are made of hard chilled iron.

From the pan mills the material is charged into *ball mills* for the final grinding upto the desired fineness. When the ball mills are very large the material can be charged direct from the jaw crusher into the ball mill.

These mills consist of a steel shell or hollow cylinder lined inside with special bricks made of *silex* stone, porcelain or rubber blocks. The object of this lining is to keep the material to be ground, out of contact with the iron casing. The mill is charged with the material together with some hard flint pebbles or porcelain balls. The charging hole is closed and the mill is made to rotate on a horizontal axis by means of a pulley or motor drive. The grinding in these mills is done by two forces, the impact of the larger balls or pebbles falling from the top to below as the cylinder rotates, and the attrition or rubbing action of the

smaller pebbles against the materials. In these mills grinding can be done both in wet or dry condition to any degree of fineness but the speed of the cylinder has to be regulated in each case. In wet grinding, the slipping of the pebbles is so great that the number of crushing blows is relatively very small. The grinding is mainly done by attrition. The speed for wet grinding is slower than that for dry grinding. The latter being

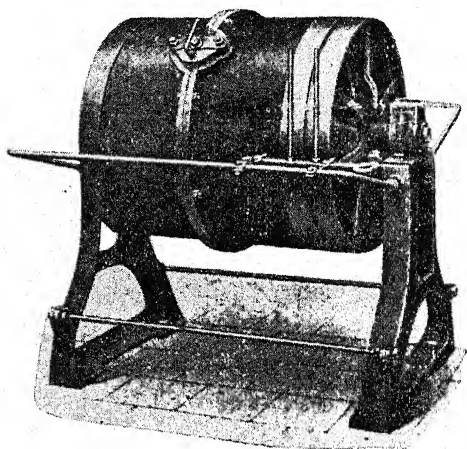


Fig. 7 A ball mill

about 1.4 times as much as the former. It is obvious from the above statement that the amount of water added in the wet grinding should be carefully controlled. In practice 30 to 35 percent of water is first added on the basis of the material charged but before discharging 10 to 15 per cent more water is added for proper flow of the ground slip. In charging the

cylinder, one third of its space is left vacant for the movement of the balls and the material. The remaining space is filled with equal weights of the material and flint pebbles or porcelain balls of different sizes. Under these conditions a ball mill having an external diameter of $4\frac{1}{2}$ feet and length 4 feet will grind a charge of half a ton of material at a time, with an

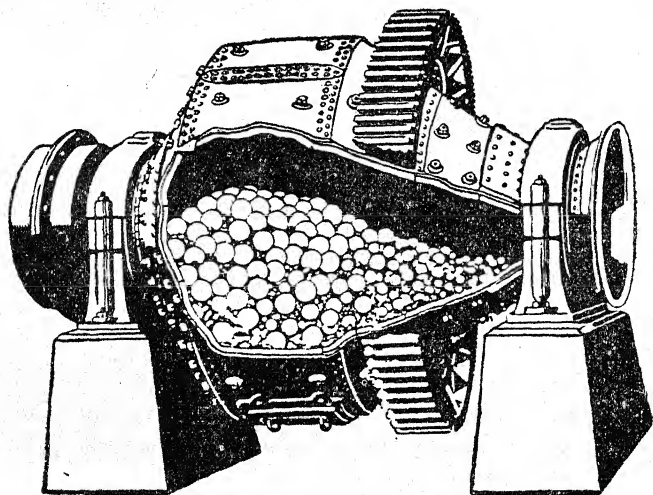


Fig. 8 Hardinge Conical Mill showing classification of balls.

equal amount of flint pebbles. The sizes of the pebbles for this particular mill should vary between $1\frac{3}{4}$ inches to $2\frac{1}{2}$ inches. The mill should rotate with a speed of 20-25 revolutions per minute. The grinding takes about 40-45 hours up to a fineness of 140 mesh.

A special type of conical ball mill known as Hardinge Conical Mill was introduced for grinding ceramic

materials wet or dry. The conical shape of this mill causes a rapid circulating and classifying action within the drum both of the grinding pebbles and the material to be ground. The coarser particles are crushed by the larger pebbles or balls which always remain near the feed end which has the largest diameter, due to the classifying action of the cone. As the particles are broken down they automatically move forward due to the slow rotation of the mill. The finer particles are then subjected to further reduction by the increased attrition of smaller pebbles on account of the greater surface area exposed both of the pebbles and the material. This automatic classification of both the material and the grinding elements proportions the energy expended to the work required which increases the capacity for power expended over other types of ball mills. Sizes range from 2 ft to 10 ft with capacities from few pounds to 50 tons per hour.

After the materials have been ground to their respective fineness, they are kept in separate tanks in the liquid or slip condition, each slip being made to a definite consistency so that during subsequent mixing of different raw materials their individual proportions may be calculated as described [in XII chapter. It has been found by practice that all the ground materials can not be kept in the same slip consistency as they either become too thick or settle down soon. For example the best consistency of ground flint or felspar as found by practice is about 32 ozs to a pint and that of china clay and ball clay are 26 and 24

ozs per pint respectively. The mixing of the different ground materials is done in a separate tank known as the *mixing ark* which is fitted with mechanically rotating paddles. This method is known as the *wet method*.

In the *dry method*, the raw materials from the pan roller mill are weighed in the dry powdery condition and charged into the ball mill for final grinding, the clay is added at the end so that the ball mill serves both as a grinder and a mixer, specially in small works, but in larger ones separate mixers are used for mixing clays with the other ground materials.

After proper mixing the slip is passed through an electromagnet in order to remove the iron particles that might have got mixed up during the previous operations. Any iron compounds obtained from the clay used is also removed by the electromagnet. These iron bearing particles if not removed at this stage would cause brown specking on the white ware. Now the slip is ready for de-watering. This is done in a *filter press*.

Filter presses are appliances for de-watering the clayey slip under pressure and making them stiffer for further use. The old pattern wooden presses are now replaced by modern iron presses. These presses consist of several cast iron discs or trays, grooved inside so that when they are pressed together, every two trays form an enclosed space called a chamber or compartment. Inside each such compartment is hung a pair of strong cotton cloths which form a bag inside each pair of trays when they are pressed together.

The clay slip is pumped through a central aperture in each tray each cloth being pierced at the centre and fixed against the tray by means of a filleted tube. The slip is pumped into the chambers by a special force pump and the water forced out through the filter cloths leave the clay as pressed cakes suitable for the next operation.

As the clayey slip is forced into each chamber the solids in suspension are arrested by the filter cloth and retained upon its surface in a thin layer which gra-

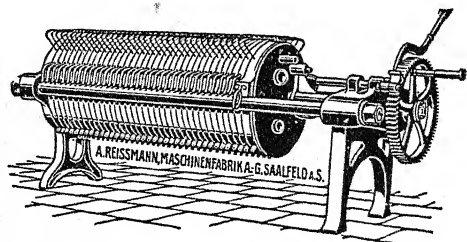


Fig. 9 A filter press.

dually increases as the filtration is continued. This process taking place on the cloth on both sides of the chamber, the two layers gradually approaching each other, finally meeting in the centre of the chamber. When this occurs, no further space is available for the introduction of the slip and the double thickness of the solids is compacted into a cake. The rate of filtration depends primarily on the force applied by the pump but mainly on the nature of the material to be filtered, because the actual filtering medium is the layer of the

solids through which the liquid has to pass. If the clayey mixture is open as in the case of porcelain bodies, the rate of filtration is rather quick and the cakes may be made thicker and harder but in the case of bodies containing ball clay or fireclay the solid layer deposited on the filter cloth is less pervious to the liquid and the rate of filtration is slower. In such cases the rate may be accelerated by using some flocculating agents in the clay slip.

After several operations, the filter cloths must be washed carefully to remove the clay particles which clog the pores of the fine cloths. The cloths should also be preserved from rotting, by soaking them occasionally in a weak solution of carbolic acid.

The de-watered cakes of clayey mass that come out of the filter press have the consistency of thick paste which are treated subsequently according to the method employed for shaping the wares.

For the plastic methods of shaping, the clay mass or *body* as it is called at this stage is sent to a kneading machine or a pug mill. The main functions of these machines are to press the body so as to squeeze out the air bubbles enclosed within the mass and to make the consistency of the body homogeneous specially with regard to the water content. The workability of the body is also greatly improved by this operation.

A kneading machine consists of a pair of steel rollers rotated by a horizontal axis and three pairs of smaller rollers rotated by vertical axes over a platform on which the clay body is placed for kneading.

The upper rollers press the body down which when passing between the vertical rollers is pressed upwards. This alternate up and down pressings remove the entrapped air from the mass and make it homogeneous, one operation taking about 45 minutes. This machine is specially suited for preparing porcelain bodies which are less plastic than earthen ware or stone ware bodies. For more plastic bodies containing ball clay or fireclay a more powerful pug mill is used.

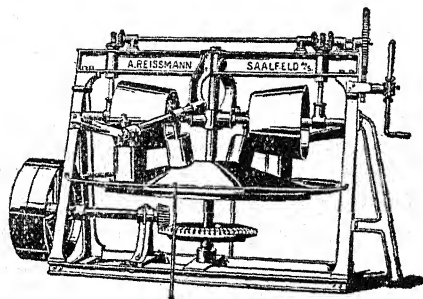


Fig. 10 A clay kneading machine.

A pug mill is a large cylinder made of several castings so that portions of it may be unbolted in case it should be necessary to clean it. An axle runs through the centre of the cylinder, end to end, and to it are attached blades of iron set at such an angle that while cutting the clay, they are continually pressing it forward. At the exit end of the cylinder there is a small chamber where the clay is pressed into a compact mass before it comes out of the mill as a homogeneous, compressed mass. The pug is fed from the top at one end, and the clay is cut up and

squeezed out in solid block at the other end ready to be used for the plastic shaping of the wares. If the pugmill is badly designed a serious defect arises in the clayware known as *lamination*. This trouble is largely due to the difference in speed of the clay planes moving inside the chamber at the exit side. The clay surface in contact with the metal of the chamber moves with a slower speed due to friction while the central core moves faster. This unequal speeds or movements of the clay mass develop different densities in the mass with the result that the band of clay that comes out

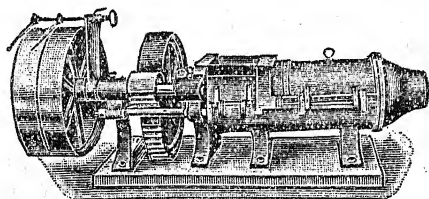


Fig. 11 A clay pug mill.

of the mill contains several lamination planes and when a section of mass from this mill is fired, cracks develop in concentric lines known as lamination cracks. This trouble has been removed to a great extent by de-airing the mass during the pugging. The mill chamber is connected to a vacuum pump so that the air which gets entrapped in the lamination planes is removed. Another method of de-airing described by Kenneth Stettinius (1937) introduces CO_2 gas in the top of the pugmill, in the region where the relatively air free press cakes are being churned and compacted. The air is displaced.

by the CO_2 gas which is 54 times more soluble than air in water at 20°C .

Besides removing the lamination trouble, de-aired clay mass produces better working property and there is less loss in drying and firing. A comparative study of an evacuated and a nonevacuated clay mass will give an idea of the advantages obtained in de-airing.

Comparative properties of a dinner ware body.

	Unevacuated	Evacuated Body.
Dry Strength. lbs/sq.in.	352	600
Drying shrinkage per cent.	3.87	3.65
Total shrinkage at cone 9.	9.72	9.6
Water absorption at cone 9.	7.86	6.6
Warpage in glazing.	0.09	0.07
Impact value.	6.97	6.08

After pugging the body is ready for throwing, or jolleying.

Throwing. This is the process of shaping claywares by hand on a rotating potters wheel. It can only be used for the making of round objects. The clay mass for throwing should be stiff enough for the article not to lose the shape, under its own weight, yet it should be soft enough to yield easily to the pressure of the hand. Good throwing is of highest importance as the defects arising from any inequality of pressure of the thrower's hand do not show themselves before drying or firing. A thrower should observe the following rules:

He should not use too plastic a clay or apply unequal pressure to different parts of the same piece.

He must graduate the vertical movements of his hands to the rotary movement of the throwing wheel so that the distances between the spiral turns on the clay should be as small as possible.

Potters wheels are of two kinds. Those which are driven by the thrower himself or by his assistant, and those which are mechanically driven. The simple potters wheel of the first kind consists of a vertical spindle, the lower end of which rests on a wooden board provided with a pivot, the upper part being secured by a collar fastened to a table. This spindle is surmounted by a small disc called the wheel head, and at its lower end, it has a heavy solid flywheel which the workman sets in motion with one of his feet. The thrower sits on a small inclined board placed near the level of the table and can rest his feet, when the wheel has the desired speed, on another inclined board.

When large or very accurately shaped pieces have to be thrown a steady running of the wheel is necessary and for this purpose another kind of wheel, similar in principle to a hand spinning wheel, or *Charka*, can be used. This modification, however, requires an assistant, and a certain amount of skill is necessary to regulate properly the speed of the wheel to the requirements of the thrower.

For large outputs, especially when great accuracy is not required, hand driven wheels are replaced by power driven ones. When constant changing of speed

of the wheel is required by the thrower, these wheels are not so convenient as the hand driven ones, although it is possible to vary the speed of these wheels either by alternating the diameter of the pulleys or by inserting intermediate conical drums.

Throwing is always followed by turning where accuracy is essential. There are several advantages of thrown and turned wares. They do not contract much in drying and have neater and more accurate appearance. They are stronger than machine made wares and in cases of big articles such as high tension insulators, throwing is absolutely necessary. If only a few pieces of one kind of article are wanted, the thrower can at once make them cheaper. Most of the fancy articles are often made by throwing.

Turning. It is the process of shaping on a lathe when the body is wet and is employed when accuracy of form is wanted and also for making articles of a lean body which must be made thick in the previous operation, because of the feeble cohesion of the clay.

Before the body is fit for turning, it must be sufficiently hard to withstand the pressure of the process, yet soft so as to allow the finger-nails to make an impression. The best stage for turning clay articles, is, when the shavings from the lathe come off about 2 to 3 inches long. To produce the desired consistency, articles to be turned are kept in a cellar or other cool places having a constant high humidity.

Both horizontal and vertical lathes are used for turning pottery wares. The tools are small blades of

steel of various shapes generally fixed to the wooden handle of the lathe, but expert turners prefer to manipulate them freely, with their hands. The pieces are finished by polishing with a blade of steel or horn, while still on the lathe.

In turned wares, bad workmanship should always be avoided. If sizes or shapes are wrong, they are at once perceived, but it is very difficult to detect wreaths which are caused by moving the tool unevenly and irregularly on the wares. After the polishing these wreaths disappear, only to reappear after the firing, no matter how carefully the polishing has been done.

A good deal of embossed decoration is obtained by the use of 'rollets' of different patterns, pressed against the articles as they revolve on the lathe, and they will be found to work best when oiled with a little turpentine.

Jolleying. It is the process of shaping claywares by fixed iron tools and a rotating mould. In this method only round and oval articles can be made. The mould is made of plaster of Paris and fitted in a cup shaped vessel known as the jigger head.

A *jigger* consists of a vertical shaft similar to a potters wheel, having a cup shaped wheel-head which receives the mould. These jiggers have a constant speed, generally power driven, and with a foot brake to start or stop the machine at the will of the operator. The iron tool that gives the shape of the articles and

known as a *profile* is attached to a handle called the jolley.

A *Jolley* is a device for carrying a profile in such a manner that it can be applied to the exterior or interior of the mould revolving on the jigger-head. Jolleys are usually of two types.

- (a) Those consisting of an inclined arm with balance-weight, and mounted on a pivot. The end of the arm opposite to the weight is provided with a slot to which the profile is attached.
- (b) Those consisting of an upright frame carrying two or more pulleys from which are suspended a vertical steel rod and a counter-poise. The rod passes through guides which ensure its accuracy of movement, and at its lower end is a device for attaching the profile.

These machines are in general used for making jugs, pails, chambers and other bellied wares.

Profiles are thick sheets of iron or steel bevelled at one edge and of such shapes as to press the body against the mould, and give the proper shape required to the wares. Profiles are to be kept accurately true; and for this purpose a sketch book is kept where the outlines of the profiles are preserved, and when their edges get worn out in working, they are filed true again.

Profiles, used in England for making earthenware, are generally 0.9 to 1.0 cm. thick, but those used in the Continent for shaping porcelain bodies, are not more than 0.5 cm. in thickness. This difference is due to the different nature of clays used in different places.

Earthenware bodies contain a lot of very plastic ball clay and unless the profile is made extra strong, it may shake during operation and cause difference of pressure on the jolleyed wares which may lead to cracking ultimately.

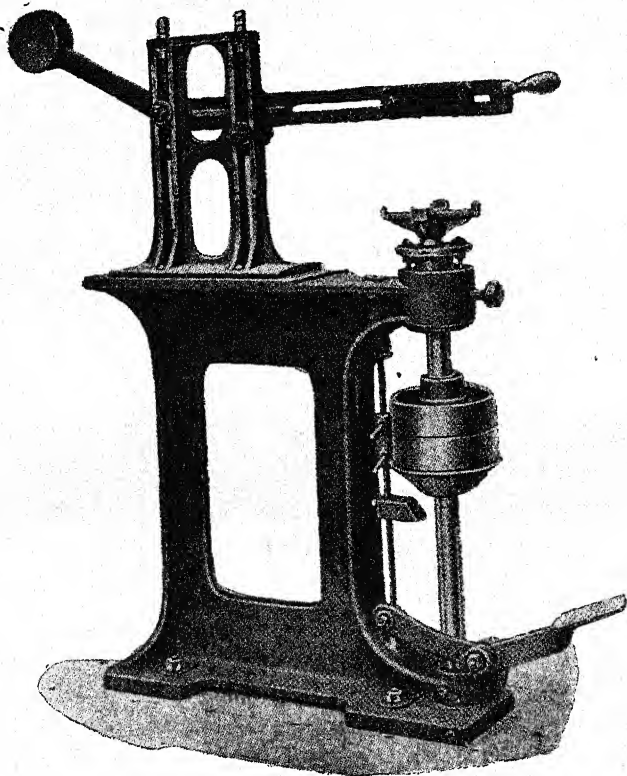


Fig. 12 A combined Jigger and Jolley.

In the process of making, a lump of clay or body is placed in the mould which is rotating rapidly on the

jiggerhead. The profile is then lowered slowly by means of the jolley handle. The profile cuts and throws out the extra clay leaving a coating of proper thickness of the clay on the mould. The mould is taken out of the jigger head and allowed to dry when another mould is placed on the jigger head and the operation repeated. For making flat articles like saucers and plates, a 'batt' or flat disc of clay is first made on a separate machine. This batt is then put on the mould, pressed with a wet sponge to drive out the enclosed air between the mould and the batt and the operation proceeded with.

When the body is very lean, such as a porcelain body, it is often necessary to use a wooden ring covered with a stretched skin or canvas on which the batt is made. In order to prevent cracking in lifting, the batt is removed with the ring and slowly inverted on the mould.

Hollow wares, such as cups, small jugs, and basins are made inside the mould, the profile forming the inner side of the wares. The same process is followed as in the making of flats but a little more care is required in handling the tools, so that the profiles come out of the pieces, without touching the sides. For making pieces with big bellies and small mouths such as chambers, big jugs and jars, the upright jolleys are most useful.

Pressing. For pressing articles into shapes, the bodies used are of three different kinds according to

their water content. These are known as plastic, semi-plastic and dry bodies.

Plastic bodies are used for making such articles as cup handles, refractory crucibles, roofing tiles, decorative bricks etc. Cup handles and other similar small articles are made in plaster or baked clay mould. A lump of plastic body is placed between the two halves of the mould and the excess clay is squeezed out by hand pressure. In making bigger articles as roofing tiles, metallic moulds lined with plaster are used. When the two parts of the moulds rest on each other, the space between them corresponds exactly to the form of the article. A batt of plastic body about the same size as the tile, but slightly thicker, is laid between the two halves of the mould and the excess clay is squeezed out. The mould is emptied by removing the upper part and turning the lower part up side down. Decorative bricks and such other heavy articles are made in two successive processes. Firstly, the bricks are cut into the proper size by a piece of wire and then they are pressed to their proper shape in a screw press containing dies of different patterns.

The semiplastic bodies are used for making small electrical articles out of lean porcelain bodies. The lean body is first dried, powdered, and then mixed with proper amount of water and oil. When the clay contains lime, the oil may become saponified, forming a calcarious salt on the surface of the dried articles which after firing form whitish patches or scums on the wares. To avoid this trouble mineral

oils which do not contain fatty acids must be used. If no oil were used the body would not be plastic enough to be worked with hand presses, and with too much water, the mass would stick to the dies. A solution of soft soap with a little kerosin oil has proved very successful in this respect.

The presses used, are either pillar press or screw press, according to the size of the article. The dies are made of steel or cast iron as great amount of pressure is required in this process and also there are many complicated articles where screws are to be cut in the articles in a single operation with pressing.

In the dry or dust pressing of articles such as flooring or wall tiles, there must be a more powerful compression as dry and powdery materials do not flow readily under a low pressure. The air between the grains of a dry body cannot entirely make its exit during pressing. Hence dry pressed articles are not so strong before firing, and require more careful handling. Moreover, if due to carelessness or insufficient pressing, air bubbles are left imprisoned, the ware may separate in layers, or the shape may get deformed after firing in the oven. These troubles are somewhat eliminated in modern practice by evacuating the air from the dies while the body is being pressed. The various advantages derived from the dry pressing method may be summarised as follows.

Dry pressed articles give sharp edge and accurate shapes. As there is very little shrinkage in dry pressed articles, odd shapes can be made without the fear of

drying cracks. No drying is necessary for these articles, hence they are fired directly. A higher temperature of firing is necessary for dry pressed articles to get the same properties as obtained from a similar body shaped by the plastic or semiplastic process.

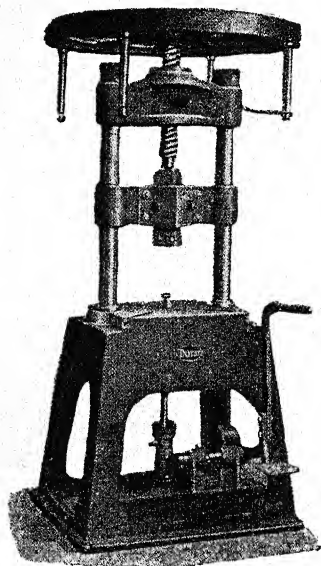


Fig. 13 A Hand tile press.

Casting. It is the process by which clay articles are shaped by filling a plaster mould with liquid clay body or slip. After a certain period the excess liquid is poured out, when the inside of the mould will be coated with a layer of the slip, a portion of

water having been absorbed by the plaster. By leaving the body in the mould until it has become sufficiently hard, it can be delivered out of the mould and an article obtained, reproducing exactly the form of the mould.

For casting less skilled labour is employed and lean clays can be used with advantage. If the clay used for making casting slip is too plastic, it would form an impermeable coating on the inner surface of the mould and the absorbing action of the plaster would be hindered. Cast pieces are lighter and less strong than pressed or thrown ones, as the former are more porous. Also, cast wares have greater contraction in firing than pressed, or jolleyed articles. Many complicated patterns can be cast with ease where other processes would be too much troublesome or even impossible, but casting process require a large number of moulds which rapidly wear out in use.

The length of time the mould remains filled with the clay slip depends, on the plasticity of the body, on the absorbing power of the plaster, and its dryness, and finally on the thickness of the article to be produced. The time can be shortened, specially for very heavy and thick casting, by surrounding the mould with an air-tight cover and then creating a vacuum around the mould, or by applying a constant air-pressure inside the mould.

When more than one kind of slip is used for decorating purpose, the coloured slips are first applied,

on the mould, with a brush and then the normal slip is poured in the mould in the usual way.

It is not an easy task to prepare a good casting slip for the particular purpose. In fact the peculiar property of the individual clay used has to be carefully studied before a slip can be made. The usual control of casting slip is through specific gravity and viscosity measurements. The viscosity is controlled through the use of alkaline salts, while the specific gravity is dependent on the ratio of water to the clayey mass. Temperature of the slip is also an important factor. It has been found in practice that higher temperature increases the fluidity of the slip. The effect of ageing is different with different salt; with carbonate of soda ageing increases the fluidity over a certain period but slips high in silicate of soda set on standing due to localised coagulation. Tannic or gallic acids have been shown by Schramm and Hall to act as protective colloids to prevent the setting of slip on standing.

Sodium silicate and caustic soda are found to be much more effective reagents to produce a decrease in viscosity of the clay slip than sodium carbonate. If soda carbonate is used alone, the slip has a high surface tension and the stream of slip poured into the mould breaks into numerous drops and this fault is known as *balling*. This may cause the entanglement of air bubbles inside the clay and cause damage to the wares.

If soda silicate is used alone, the slip becomes *stringy i. e.* flows in strings, like thick syrup. A proper

balance between these two effects is secured by using a suitable mixture of these two reagents. The slip will then pour in a clean cut solid stream without any tendency to draw air bubble. For earthenware bodies, a good casting slip can be prepared by adding about 0.3 per cent of alkalies made from equal proportions of soda carbonate and soda silicate. But for thick casting of sanitary wares larger proportion of silicate should be used. It makes the cast wares hard and dense. In clay bodies where no ball clay or plastic fire clay are used the amount of silicete should be increased at the cost of the carbonate to get better casting property.

In clay blunging, the first few hours, is a very important period when changes occur inside the clay slip, and if the clay is not thoroughly blunged during this period, specially after adding the alkalies, the slip will not be homogeneous and cause trouble in casting. If casting slip is exposed to the atmosphere for a long time, CO_2 in air forms a skin on the surface of the slip, which when broken and mixed up, forms a sort of brownish patches on the sides of the cast wares.

Finishing. This process consists of a series of manual operations in order to make the ware ready for firing. It has always two principal functions.

- (a) To unite the different parts of the articles when they have been made separately in one or different processes.

- (b) To correct any imperfection in the shape and to clean the articles.

It has been already stated that articles such as teapots, teacups etc. are made in parts. These different parts are united by means of the same slip out of which the articles are made. Joining should be made when both the parts are in the same moist condition and also not too dry. If joined in dry condition the joint would crack in firing if not in drying.

The imperfections in shaping chiefly occur at the seams of the moulds both in pressing and casting. These seams are removed by a small knife and the marks are sponged with a wet sponge. If there is any correction to be made such as cavities and hair cracks which have arisen during the moulding, these are made up by means of a small quantity of slip. Plates and saucers are *fettled* or polished when they are dry, on a whirler first by means of emery or sand paper and finally with a piece of flannel. Cups and other hollow articles are only sponged, in the damp condition.

Drying. The complex movements of water and solid particles during the drying of claywares are not yet very perfectly understood. Many faults attributed to drying may be traced back to other causes. A square slab of clay may dry oblong and the circular piece may dry oval, but these phenomena are mainly due to the 'grains' developed in the clay body during the pugging operation. It is well known that clays

exhibit a greater contraction when subjected to mechanical or gravitational stress either before or during drying operation, so that in a large block the vertical contraction is greater than the horizontal contraction.

During drying, the surfaces of the articles first lose a certain portion of water by evaporation, which is replaced immediately by water carried from the interior of the articles by capillary action, and this process continues until the centre of the mass is dry. So long as there remains in the body a sufficient quantity of water to allow the particles of solid matter to be displaced, the latter collect together, filling up the spaces created by the departure of water particles which separate them. This causes a contraction of the articles roughly equal to the volume of water lost. When there is no longer sufficient water between the solid particles to allow them to move, a further elimination of water from the body produces pores between the solid particles, and this process goes on until the whole of water is evaporated. Thus we can divide the process of drying into three stages.

In the first stage of drying water is evaporated rapidly from the surface of the articles, this water being replaced from the interior by capillary action. Whatever factor helps this diffusion of the internal water, favours rapid drying. If the clay is very plastic, the colloids present in it choke up the internal channels and retard the rapid diffusion of water from the interior to the outer surface. This choking up of the passages may be improved by use of acidulated water.

Lovejoy (1933) has shown that about 60 per cent of the total water content of a stiff mud clay ware is eliminated by the surface evaporation. This water is termed as *shrinkage water* as the shrinkage of the ware at this stage is very nearly equal to the volume of water lost. At the end of this stage the body is said to be *Leather hard* and fit for turning, and joining.

In the second stage of drying the diffusion of water from the interior slackens down so that the rate of evaporation of water tends to be greater than the supply from the interior, resulting in the development of pores inside the body. If the body is not very compact the evaporation takes place from below the surface of the ware so that the slow shrinkage that takes place at this stage is regular throughout. In the case of a dense and heavy ware the quick surface evaporation causes unequal shrinkages between the top and interior layers of the ware setting up strains in the body which results in drying cracks. This strain can be removed to a great extent by the humidity drying system. At the end of this stage the colour becomes lighter and the body is said to be *bone dry* and fit for firing.

In the third or end stage of drying when the fine particles of clay are completely jammed together so that they become immobile, the loss of water is not attended by any further shrinkage excepting that which may be due to the contraction of the colloidal matter in the clay. Hence the increase of porosity developed at this stage is very nearly equal to the loss of water.

Artificially heated dryers are required to complete this stage but in majority of cases this stage is attained in the oven during the *water smoking* period.

An idea of the relation of water content and shrinkage of a clay body can be had from the following diagram given by H. H. Macey (1934).

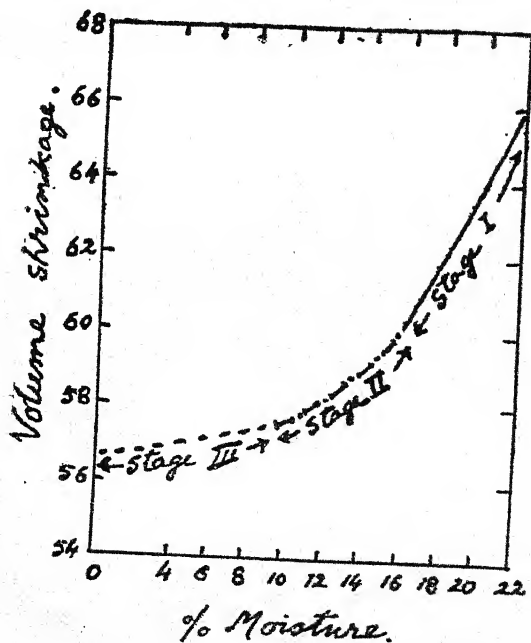


Fig: 14 Drying shrinkage of a clay body.

In order to prevent cracking or distortion of shape during drying of claywares the two factors to be considered are, to increase the diffusion of moisture from within to the surface of the ware and, to control

the evaporation from the surface. In many clays specially rich in colloidal matter, addition of acids or salts have been found to be beneficial. An addition of common salt up to one per cent renders workable many clays which crack badly in drying. It also improves the firing property of the clay by increasing the vitrification period, that is to say, the clay will start to vitrify at a lower temperature and will not get over-fired at the temperature when untreated clay is liable to get distorted. Hussain (1930) showed that an addition of one per cent of hydrochloric acid in a clay reduced the drying loss from 13 to 3 per cent. This improvement is due to the fact that acids and acid salts flocculate the colloidal substances in the clay and improve the capillary action so that water is easily diffused to the surface. Lovejoy (1933) has shown that flocculating with an acid in a normal clay does not increase the flow of water and he observed that this method will be beneficial in a clay so highly colloidal that the pores and capillary tubes are clogged easily.

Temperature and speed of air also play important parts in the progress of drying. The viscosity of water at 50°C is only half its value at 20°C. Hence the speed of drying at the higher temperature will be nearly double. At 100°C the drying power of the hot air is more than 20 times than what it is at 20°C. Bigelow found that if the rate of evaporation in calm air be taken as 100, the rate would increase to 107, in a mild wind of one kilometre per hour, and to 114 in a wind of two kilometres per hour. When we have a fixed amount

of heat available which can heat up either one volume of air from 60°C to 100°C or four volumes, from 60° to 70°C , it has been calculated that the larger volume of cooler air would have only one quarter as much drying power as the smaller volume of hotter air.

The rapidity with which drying can take place depends mainly on the texture of the body and the shape and thickness of the articles. As the speed of drying is greatest at the first stage, it is sometimes found advantageous, to cover the articles at this stage, with a damp cloth, or to invert the moulds containing the articles so as to prevent too rapid drying, which may lead to distortion of shape or rupture. When the drying is rapid, the shrinkage is less, than when the drying is slow. Thus, of two articles made of the same body, the one would shrink about 6 per cent when dried in 24 hours, while the other shrinks 7 per cent if dried in 120 hours.

The contraction of a clay body during drying also depends on the amount of water used during formation. If a body is made up with 10 per cent water, its linear shrinkage would be about one per cent but if the same body is made up with 25 per cent of water, the linear shrinkage would increase to about 10 per cent. Thus, a cast body would shrink more and be more porous than a jolleyed one. Articles with large surface area would dry in less time. Thus, a solid brick would take much more time in drying than a hollow or perforated one.

When an article consists of both thick and thin parts, the thin parts such as the corners and edges, dry more rapidly than the thick parts and offer resistance to the latter. If the tension is too great for the mass to resist, ruptures or cracks will arise. It is therefore advisable to avoid any abrupt passage from a thick to a thin shape in the same article.

The actual method of drying depends on the particular condition. In the clay washing plants, the washed clay is dried on open hearths heated by coal fire. In earthenware factories, waste steam from boilers is used to heat up the driers. In porcelain factories, brickworks, and other potteries, where heavy articles are manufactured, the waste heat from ovens is utilised for drying the wares. Heat is drawn from the ovens through large pipes and distributed all along the drier. The radiated heat from continuous chamber kilns is utilised for drying the wares on the top of the kilns. In modern tunnel driers, both humid and hot current of air is used for rapid drying without any danger.

In hot countries like India artificial drier can be dispensed with for normal manufacture, except during the few months of rains, when the waste heat from the ovens can be conveniently employed.

Humidity Drying. When a wet clay body is allowed to dry in hot air, the evaporation takes place from the surface with the result that the surface layer contracts more than the interior. This unequal shrinkage causes cracking or *checking*. Checks are

small surface cracks, which indicate a different set of conditions between the surface and the interior. A very clear analogy is the crazing of glazes, explained in a later chapter. Ordinary cracks on drying generally occur perpendicular to the outer surface going towards the centre of the mass, whereas checks occur along the surfaces of the ware and do not go deeper than the surface skin formed due to quick evaporation from the surface layer. The surface shrinkage of a clay-ware can be avoided if the evaporation is made to take place from the interior of the ware. This is effected inside a closed dryer by introducing hot steam so that both the temperature and humidity of the drying air are raised. The high surrounding humidity prevents evaporation from the surface until the interior temperature is raised to the minimum or critical point from which drying can proceed at a rapid rate. After the critical temperature is raised inside the body, the humidity can be lowered and hot air allowed to play round the articles for rapid drying. Introduction of this system has made drying problem safer and quicker, but to get the best result the particular conditions of each clay body with the variation of shapes and sizes should be studied.

Scumming. It is the universal bug-bear of the clay workers. The ordinary scum is a dirty white coating which comes to the surface of the wares during drying and becomes permanent on firing. Scumming may also develop during burning or even during use, although the trouble is commonly manifested in drying.

Common scum develops from sulphates of lime, gypsum or selenite. Ordinary water can carry about 0.25 per cent of these minerals but when carbonated, water can carry much more of these salts in solution. Almost all brick clays contain gypsum in solution. Scrapings from casting shops invariably contain some plaster from moulds, which when mixed with water is hydrated and goes into solution. Use of old press water may also introduce these salts into the clay mass.

When the wares dry slowly, the soluble salts contained in the body come out on the surface and as the water dries up, the salts get deposited on the wares. These deposits generally concentrate at the most exposed parts, such as noses and ears of figures, edges of cups etc. These deposits or scums are generally removed during the finishing process. If the rate of evaporation is greater than the supply of water from within the wares, the drying will take place below the surface of the wares and then there would be no scum deposited on the wares.

Scums often develop in the dryer when combustion gases get into it, either directly or by leakage. If the clay contains lime carbonate, it is converted into sulphate by the sulphur gases in a humid atmosphere. The sulphate gets dissolved and subsequently in the dry state can be easily removed but when once fired, become permanent blotches on the wares and when subsequently glazed, the glaze may drop off from where there were scums.

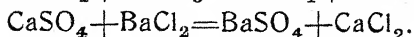
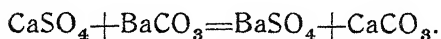
Scums may also develop during firing even when no scums were formed in drying. At the beginning of the firing, when the kiln is still damp, the alkaline salts present in the ashes of the fuel may combine to form scum. Sulphurous fumes or acids may combine with any lime and often cause spots or scums on those parts which are most exposed to the gases.

Scumming or efflorescence may occur during use of the wares and long after firing has taken place. Efflorescence is another name for scumming, but this term usually refers to the white, yellow or green coating which appears on the finished products after removal from the kiln and often not before months or years have elapsed since the wares were exposed to the weather. If the temperature of firing is not high enough to convert the soluble salts generally present in natural clays (sulphates, chlorides, and silicates of lime, soda, potash and magnesia), into insoluble silicates, these salts may be dissolved slowly and brought to the surface by long exposure to the rains or damp weather. The white efflorescence generally found near the joints of building, may arise from soluble salts present in the water used for making mortars. Brownish scums sometimes found on bricks are due to the soluble iron salts formed by weathering of low fired bricks.

Vanadium salts produce yellow and green efflorescence, on low fired firebricks. Such efflorescence when yellow, are due to the formation of vanadic acid by the exposure of the bricks to damp. Under the

influence of coal dust, a bluishgreen colour is produced, due to the reduction of vanadic acid to oxide of vanadium.

Antiscum Mixtures. In order to prevent the scums on articles made of clay containing sulphates of soda, lime or magnesia, some antiscum mixtures are used in trade. Either barium carbonate or chloride, or both may be used for this purpose. The sulphates and barium salts undergo a double decomposition forming insoluble barium sulphate and carbonates of soda, lime or magnesia.



Although a soluble salt by itself, CaCl_2 does not form any scum or efflorescence.

In general practice, the greater portion of the sulphate is removed by barium carbonate and the remainder by a little quantity of barium chloride, as an excess of the latter may itself form a scum. It is only precipitated barium carbonate that works satisfactorily for this purpose. Natural carbonate—whitherite, does not work well. Barium chloride being soluble in water reacts easily and can be employed alone with advantage where only a small amount is necessary.

In a German patent, an organic coating is applied on the surface of the wares, specially bricks, on which the scum may form. This coating burns away and the scum drops down with it.

When the scumming is due to the presence of pyrite in the clay the sulphur can be roasted out by

careful burning and the sulphates destroyed by reducing action. The danger from pyrite is largely over when the water smoking is finished. Sulphur in coal can be fixed by adding some lime water in the coal which removes the sulphur with the clinkers.

Moulds. These are perhaps the most costly part of the potters stock-in-trade. There must be moulds of every size, and shape, from the elaborate vase to the simplest saucer. They are made in one or more parts, as may be necessary for the manufacture of the piece. Plates and flat working moulds are generally made in one piece whereas sugar boxes, ewers etc are made in several parts.

Moulds used in the pottery manufacture are generally made of *pitcher* or fired clay; and plaster of Paris. Moulds made from former give very clean, clear impressions, and last considerably longer in good condition than those of plaster, but they have two defects. Firstly they cost considerably more in the first instance and secondly, they are only slightly absorbent; and for this reason a much larger quantity of pitcher moulds is required than those made of plaster. Pitcher is still, however considerably used for cup handles and such other small articles, and also for leaves, garlands and such other ornamentations which are afterwards applied to vases made of Jasper and Basalt bodies.

Plaster is now the universal material for making potters moulds, on account of its great absorptive power and the facility in working. The plaster used

should be good, superfine plaster of Paris and it should always be stored in a dry place before use. Moulds would be much harder and their lives considerably increased if no plaster were used earlier than 10 to 15 days after boiling.

Moulds are made from a model representing exactly the article to be made, but slightly larger, to allow for the shrinkage in firing. Models are either made from wet clay or plaster. When models are made of round pieces such as cups, jugs, electrical insulators etc. it is better to have them made of plaster ; but for making models of complicated shapes and with ornamental designs, clay is preferable.

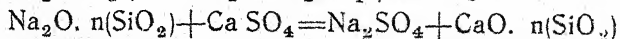
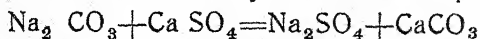
The first mould obtained by casting from the model is seldom used for moulding. This mould is called the *block mould* or *master mould*, and is only employed to make the *casings* as they are called by the mould makers, which are the reproductions of the models. From these casings working moulds are cast. Moulds should be thoroughly dried before being put to use and they last much longer if they are dried systematically between regular work. They should be dried at low heat and longer they dry at lower temperature, the better for the life of the moulds.

In making working moulds out of a casing, first clean all dust from its surface and if it is too dry, just dip it in a tub of water for a few seconds. Then 'size' it thoroughly with an emulsion of soft soap solution with a wet sponge and keep the casing ready on the table. Mix three parts of plaster with one part of

water by weight, and stir till it begins to set. It takes about five minutes for this operation. Pour the plaster slip into the casing with a circular movement and shake the liquid well to drive out all air bubbles arrested between the casing and the slip of plaster. Allow the plaster to harden. It warms up and when it is cold again, take off the mould from the casing. The mould is then scraped clean with an iron knife and any marking or number written on it.

Moulds are made hard or soft according to the purpose for which they are made, by using more or less plaster with water. Casings are generally made hard. Moulds for casting are made softer than those for jolleying or pressing.

When plaster moulds are stored for a long time specially in a damp place, it is found that their surfaces are coated with a white fur-like substance which on examination is found to contain a considerable quantity of sodium sulphate, derived partly from the soluble salts in the clay, partly from the solubility of plaster in water, and in part from the decomposition of soda carbonate and silicate by the calcium sulphate.



The presence of such matters as soluble phosphates increase the solvent action of water on plaster of Paris and this explains why the casting surface of bone china moulds do not last so long as those of earthenware. Growing crystals of sodium sulphate (Glaubers salt) exert a great pressure on plaster moulds which

are stored in a damp room and make them rotten. The effect of pressure of these crystals can be experimentally determined. If a solution of this salt is poured in a crazed earthenware vessel, the solution will gradually work its way into the porous body and in a couple of weeks the whole vessel will be rotten and shatter to pieces by a slight shock. This explains why moulds stored in a damp place for long time are often found to become rotten, and break down during working.

Principles of Firing. Pottery wares, except hard porcelain, the finest and noblest of all ceramic wares, are results of arrested reactions. The firing is not continued to develop the full pyro-chemical reactions inside the body but checked at different stages for different kinds of wares. The firing of terra cotta wares is arrested as soon as the clay has hardened sufficiently, while fine earthenwares are fired up to the stage of incipient fusion of the particles. Stonewares and soft porcelain bodies are vitrified more or less completely so that the latter show some translucency when seen through transmitted light.

The effects of heat on pure china clay have been discussed in the previous chapter but when the clay is impure or is mixed with other minerals the reactions are rather complicated. In order to understand the reactions which go on inside a clay body while it is being fired, the whole period of firing may be divided into different stages but it should be understood here that these stages do overlap with one another because

it is impossible to make a temperature division which will separate two classes of reaction, which may take place simultaneously.

1. *Smoking or steaming stage. Up to 150°C.*

Strictly speaking this stage should be included in drying. During this period any water of formation which has not been previously driven out in the drier together with hygroscopic moisture, are got rid of. The object of the fire man is to remove this water as rapidly and as completely as possible, without damaging the goods; sufficient time being allowed to effect the evaporation of the water without causing it to boil and so spoil the surface of the wares. If the heating is imperfectly carried out, the goods are apt to fly, or unpleasant condensation products are formed on them. The water vapour, if not driven out of the oven as quickly as they are formed, would condense on the saggars or the wares inside them, as a fairly strong acid, chiefly owing to the sulphurous gases produced by the oxidation of sulphur present in the coal. As the air passing through the kiln during this smoking period is the chief agent which carries away the steam and other volatile matters, it is necessary to allow sufficient passage of the same during this period. The name smoking or steaming is derived from the facts that during this period the firing is never bright and the oven is full of steam derived from the damp goods. The period of smoking varies greatly according to the nature of the goods. Dust pressed tiles which are not dried before firing generally take 40-50 hours, whereas

porcelain goods with open bodies require only 5 to 6 hours for this purpose.

2. *Decomposition stage.* 200-500°C

As the temperature rises above 200°C, the volatile organic matters begin to decompose, and any hydrated oxide of iron present in the clay, begins to dehydrate and the sulphides decompose. The rate of firing of the oven at this stage, may be sufficiently increased provided the clay does not contain much hydrated iron oxides or organic compounds. When the temperature inside the oven is about 500°C or the oven just begins to become red, the firing should be again slowed down.

3. *Dehydration stage.* 450°-600°C.

At this stage the chemically combined water of the clay substance, begins to decompose very rapidly and if the firing is not slow, the wares may get damaged. At this stage, the clay is very liable to absorb gases and susceptible to the actions of acids. The amount of water vapour given out from the wares in an earthenware biscuit oven at this stage, has been estimated to be about 50 times the volume of the oven and this vapour must be cleared off with plenty supply of air, otherwise the oxidation of the carbonaceous matters present in the clay will suffer greatly, as carbon can not be fully burnt off except by direct contact of air with its particles.

Carbon may be present in the clay as anthracite which burns off easily without causing much trouble. Bituminous carbons contain much hydrocarbons and also some oil, which produce local combustion and

hinder the oxidation of the clay. Lignite carbons produce lot of steam but do not give so much trouble as the former one. If a fire clay is removed from the oven at this stage, it would be found to be of blackish to grey colour depending on the amount of carbonaceous matters present in the original clay. The clay has lost its power of becoming plastic on treatment with water, but it has not yet become sufficiently hard and strong to be durable.

4. *Oxidation stage.* 350°C-900°C.

This period actually begins with the oxidation of the easily ignited organic matters or sulphur compounds which begins near about 350°C and continues until the last trace of carbon is burnt out at the high temperature of over 900°C. It therefore overlaps the dehydration period and in some cases infringes also on the next stage.

Iron sulphide FeS_2 when present in clays begins to decompose to FeS at about 400°C but it requires a much higher temperature of about 800°C to convert FeS into oxide of iron. The sulphur gases produced from the claywares at this high temperature can not do much damage if a good draft is created to remove the gases quickly. Calcium carbonate when present in the clay body decomposes into free lime at about 800°C and more. Carbon and sulphur have got greater affinity for oxygen than ferrous oxide. Hence it is necessary that both the carbon and sulphur be removed completely before the ferrous iron can be brought into the oxidised state which produces the bright red colour in iron

contained clays. If the oxidation is not properly done, the ferrous oxide combines with the silica in the clay, and if the temperature is sufficiently high, forms dark slag or spongy wares. Failure to complete oxidation of the carbon, gives rise to *Black Cores*, specially in bricks and other thick articles. The pores nearer the surface of the wares become closed with the gradual rise of temperature and prevent access of air to the centre of the articles, so that the carbon present inside the wares remain unchanged, producing dark patches, generally known as black cores.

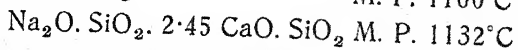
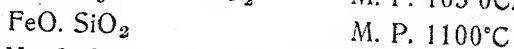
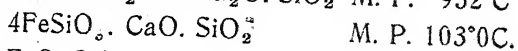
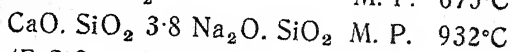
The decomposition products of the clay substance at this stage may be roughly said to be free silica, free alumina and oxides of lime, magnesia, iron and alkalis. If a sample of china clay body is withdrawn from the oven at about 800°C , it would be found, to possess a pink colour due to the separation of free iron oxides from the clay body. As the temperature, rises, the iron unites with the alumina and silica, forming a colourless body; but if carbon be present in the clay, the iron cannot unite with the alumina, until the whole of carbon is got rid of. It is the presence of free iron in the oxidised form, that gives the characteristic colour to burnt clay wares. The presence of CaO in the clay body affects the colour greatly. Lime changes the red colour into buff or yellow. If the iron is not properly oxidised the colour will darken to greenish shade.

Near the end of this period the body becomes porous due to the expulsion of the organic matter and the decomposition of the carbonates and

sulphides. The external volume also increases slightly due partly to the increase in volume of the quartz and partly to the specific volume increase of the clay substance. Brown and Montgomery have shown that when a kaolin is heated to 600°C it loses about 13 percent in weight and its specific gravity drops down to 2.5. At 800°C the corresponding loss is 14 per cent but the specific gravity remains the same at 2.5. Wares at this stage is known as *Biscuit fired* and porcelain wares are often removed at this stage for glazing.

5. *Vitrification stage.* $900-1300^{\circ}\text{C}$.

As the heating progresses further some of the materials present in the body combine together and form easily fusible masses known as *eutectic compounds*. A few low temperature compounds that may form in the body are :—



These easily fusible substances melt and flow among the pores of the particles and gradually fill some of them with a cementing glass. If the ware is removed at this stage it will be found to possess good hardness, ring and low porosity. This is the stage of *incipient vitrification* and most of the pottery wares are removed from firing at this stage; but the temperature required to attain this stage is quite different for different classes of

articles. Common bricks and tiles attain this stage at about 900°C , while fire bricks require a high temperature of 1300°C or more. Fine earthenwares are finished at about 1200°C . On further heating, the glassy material attacks and dissolves more unmolten materials so that the wares gradually lose their porosity and become what are known as *vitrified wares*. Stonewares and soft porcelains are removed from firing at this stage. The amount of vitrification is judged by the water absorption of the fired wares. Good stone wares should not absorb water more than 3 per cent while fine porcelain should have an water absorption less than 0.25 per cent.

In a clay body containing different minerals there is no sharply defined temperature of melting but the fusion or vitrification continues over a range of temperature known as the *vitrification zone*. In commercial clay bodies the vitrification zone should be as long as possible so that the wares from different parts of the same kiln may be uniform in colour, size and density.

When the firing is harder the proportion of molten material would be so large that the unmolten components could not resist its softening action and the ware would lose its shape. In this case felspar glass is a better flux than lime or magnesia ones because the former has a high viscosity and does not allow the ware to lose its shape due to slight overfiring.

In hard porcelain, felspar is the only flux used. It melts into a very viscous glass between 1100-1200°C. The fluid dissolves the molecular residue of the silicic acid left after formation of sillimanite $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and then attacks the free silica in quartz, and more or less completely dissolves it, depending on the grain size, temperature and time. In fact the liquid felspar behaves like an unsaturated solution.

6. *Crystallisation stage.* 1300°C. upwards.

When the temperature rises above 1300 C a new compound is formed which is known as Mullite— $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and has a crystalline structure similar to sillimanite. The nature and amount of these crystals determine the true porcelain from the artificial or soft porcelain. In developing a true hard porcelain mere chemical composition is a less important factor, unless the firing is properly conducted to develop the crystalline structure inside the body. If the pyro chemical reactions have been complete a thin section of the body under a microscope will reveal a homogeneous glassy matrix with network of numerous small needle shaped crystals sometimes with lattice structure. A porcelain of this type is in all respects, homogeneous and in the technical sense genuine porcelain.

The duration of heating at the finishing point has a great effect on the goods fired. This prolonged heating at a constant temperature is known as *soaking* and it is very essential in order that the contents of the kiln may be heated uniformly on all sides as heat penetrates through heavy claywares but very slowly. Moreover

the temperature in some commercial kilns vary from 50° to 100°C in different parts, and it is essential to bring up the temperature in different parts to the same level by proper soaking of the kiln. Slow heating also helps in the formation of crystals which is so essential in hard porcelain.

CHAPTER IV.

GLAZES, COLOURS, AND DECORATION.

Glazes are carefully prepared mixtures of minerals and chemicals, which when applied on clay wares and heated to suitable temperatures, melt into liquid and uniformly cover the surface of the wares. On cooling, this liquid sets into a kind of glass with a glossy surface, which is technically known as the *glaze* of the ware. A good glaze should be so composed that it would adhere firmly on the ware and should not be easily affected by acids, alkalies and external shocks or abrasion. The composition of glazes vary widely depending mainly on the temperature of firing.

Hard glazes which are applied on porcelains and stonewares generally melt above 1200°C . They contain much alumina and silica with alkalies, lime or magnesia as bases.

Medium glazes as used on fine earthenwares, melt between 1050°C and 1200°C . These glazes contain less alumina and silica, some portion of the latter being replaced by boric oxide. Lead oxide is used to lower down the melting point.

Soft glazes are used on low temperature majolica wares and melt at about 900°C . These glazes generally contain the alkalies, and lead oxide with a small amount

of alumina and silica to form an easily melting transparent glass.

Some substances like oxides of tin, antimony, and zinc, and phosphate of calcium, when introduced in glazes tend to make them opaque. These opaque glazes are termed as *enamels* and are generally used on coloured bodies to cover the surface completely. The word enamel is sometimes used to denote soft coloured glazes used generally for the decorative purpose or to cover the defects of white wares, although these glazes may not contain any opacifying agent mentioned above.

Glazes, like true glass, are amorphous substances, formed of alkaline, earthy, or metallic silicates or borates, and their molecules have not taken a definite grouping together, as is found with crystallised bodies. They are said to be in the form of a super-cooled liquid, and do not possess the definite properties of a true chemical compound. If the composition of a glaze is not properly controlled, one or more of its constituents may crystallise out from the main solution and make the glaze turbid. This phenomenon is known as, *devitrification*.

As the precise constitutions of glass or glazes have not been settled, they are often stated in terms of oxides contained in the compositions. The general conventional form of expressing a glaze composition is— $RO \cdot R_2O_3 \cdot RO_2$ called the glaze formula. Here RO stands for the oxides of alkalis, alkaline earths and the divalent metals such as lead, zinc etc. R_2O_3 represents alumina and sometimes ferric oxide.

RO_2 stands for silica and often boric oxide. This method of representing the composition of glazes helps to a great extent in comparing and controlling their properties.

Raw materials used in glaze compositions, have each some particular properties of their own. Their actions in glazes are discussed in what follows.

Alumina: It is introduced in glaze composition as china clay, felspar, china stone and also as calcined alum or Al_2O_3 . It raises the fusing temperature of the glaze, prevents devitrification, and makes the glaze more resistant to the atmospheric influences. Even 0.02 molecule of Al_2O_3 , cures the milkiness of the glaze, but too much raw china clay in the glaze tends to develop cracks on drying, which may help the glaze to roll together on subsequent firing. It also tends to make 'pinholes' in the glaze. Alumina in a glaze mixture should not be more than one tenth of its silica content as it also makes the glaze less glossy and more enamel like.

Silica: It is introduced in glazes in pure form as quartz, flint, and sand, also in the combined form as china clay, stone, felspar etc. It unites with the basic oxides and smelt into a glass at the glaze temperature. High silica makes the glaze less fusible and less liable to run and soak into the porous body. Raising the silica content also makes the glaze less liable to craze or crack after firing or during use. If the proportion of SiO_2 is more than the ratio of $\text{RO} \cdot 3\text{SiO}_2$ that is a trisilicate, the glaze

begins to devitrify, particularly if the proportion of lime is high. This will consist in the separation of silicic acid or lime silicate in crystalline form which cloud the glaze and destroy the gloss of the surface.

Boric Oxide: or B_2O_3 . is introduced as borax ($Na_2O, 2B_2O_3, 10 H_2O$), borocalcite, ($CaO, 2B_2O_3, 6H_2O$), boracite ($6MgO, MgCl_2, 8B_2O_3$) or boracic acid (H_3BO_3). It shares with silica the property of combining with bases, to form glassy compounds, which with the exception of the alkaline oxides, are insoluble in water. Boric acid and silica glasses are miscible in all proportions, but the boric glasses are much more fusible than silica ones. Replacement of a part of the silica by boric oxide, serves as an excellent means of lowering the melting point of glaze without altering its composition. B_2O_3 makes the glaze more brilliant but less resistant to the influences of moisture, acids, and the washing liquids, containing alkalis in solution. It also reduces the scratching strength of the glaze. If the proportion of B_2O_3 in the glaze mixture is more than one fifth of its silica content the glaze inclines to become milky in the subsequent enamel firing. It also exerts a solvent action on the under-glaze colours.

Alkalies : These are introduced in the glaze mainly as carbonates or nitrates of soda and potash but often with other materials such as felspar, borax, Cornish stone etc. Their presence makes the glaze more fusible and high amount renders it easily attackable by the weathering influences and organic acids. Highly alkaline glazes are more liable to craze, so their proportion in

ordinary earthenware glazes should not be more than 0.4 molecule.

Lead oxide : PbO is introduced as litharge (PbO) red lead (Pb_3O_4), white lead ($3\text{PbO}, 2\text{CO}_2, \text{H}_2\text{O}$) or galena (PbS). It forms insoluble lead glasses with silica or B_2O_3 . It makes the glaze more resistant to the weathering actions. It dissolves the other constituents very quickly and the glaze is fluid enough to allow the bubbles to rise to the surface. It also gives wider margin of safety for firing. Glazes become bright and clear with lead, but high proportion of it makes them more liable to craze. A little amount of white lead in the mill mixture keeps the glaze-slip creamy.

Lime : CaO is chiefly used as limestone, marble, chalk (CaCO_3), and also with borocalcite and dolomite ($\text{CaCO}_3.\text{MgCO}_3$). It forms double silicates and borates with alkalies. It makes the glaze less fusible and the surface hard to scratch but helps the glaze to become milky by forming crystals. It also whitens the glaze to a great extent by its bleaching action. When carbonates are used, they should be fritted to get rid of the gases, otherwise CO_2 evolved may afterwards tend to cause pinholes in the glaze.

Magnesia : MgO is introduced into glazes as dolomite, magnesite (MgCO_3) talc ($3\text{MgO}, 4\text{SiO}_2.\text{H}_2\text{O}$) and also as magnesia. It is generally used for high temperature glazes. Like lime, it also whitens the glaze but if more than 0.4 molecule of MgO is added, the glaze begins to roll or collect in patches. It also affects some colours.

Baryta : BaO is used in the form of barytes (BaSO_4) or witherite (BaCO_3). It is generally used in the leadless glazes as it is nearest to lead for fusibility, but it has no such margin of safety as is found with lead glazes. BaO gives greater brilliancy to the glaze than lime or magnesia and is second only to lead.

Zinc oxide (ZnO), tin oxide (SnO_2), Zirconia (ZrO_2) and antimonates of soda and potash are used in glazes as opacifiers. The first two substances are most universally used in pottery. Zinc oxide in small quantity increases the brilliancy of the glaze but if added in greater proportions, it crystallises out from the glaze during cooling in the form of $2\text{ZnO}.\text{SiO}_2$. For this reason it is used for making mat crystalline glazes.

The fusibility of the metallic oxides or bases that yield colourless glazes are, according to Seger, in the following order :

$\text{PbO}.$ $\text{BaO}.$ $\text{K}_2\text{O}.$ $\text{Na}_2\text{O}.$ $\text{ZnO}.$ $\text{CaO}.$ $\text{MgO}.$ $\text{Al}_2\text{O}_3.$

The above oxides become less and less fusible as they proceed from left to right. The substances that easily fuse in fire and also help other materials to melt with them, are called *fluxes* in ceramic industries. It is not only the kind of flux, but also the number of fluxes used, which govern the fusibility of glazes. The fusibility increases with the number of fluxes present. In order to produce a transparent glaze, it is necessary to have at least two fluxes, one of which is as a rule

an alkali. The order of fusibility of colouring oxides according to the same authority is as follows :

CuO , MnO_2 , CoO , Fe_2O_3 , U_2O_3 , CrO_3 , NiO .

Fritting. When the glaze materials contain soluble salts like alkali carbonates or nitrates, borax etc, these salts are liable to get dissolved in water and separate out from the main mixture. In order to obviate this difficulty, those soluble salts are made insoluble by fusing them together with some silica, lime or lead oxide, according to the composition of the glaze. This fused glass-like mass is termed in pottery as *frit* and the process of fusing is termed as *fritting*. The remaining insoluble portion of the glaze mixture, is added to the frit and ground together with water.

There are several other advantages of fritting the glaze mixture and these can be stated as follows :

- (1). It minimises the difference in densities of the various constituents of the glaze and so reduces the chance of their settling down separately.
- (2). It drives out the CO_2 and other gases and overcomes some of the heat work to be done by the glaze firing which is so essential in modern electric fired tunnel kilns.
- (3). It diminishes the solubility of the glaze in acids and minimises lead poisoning. Certain forms of lead salts such as white lead and lead sulphide are more soluble in human gastric juice than other lead compounds. These weak-acid soluble lead compounds produce lead poisoning as our system can not clear off these lead salts

as easily as it does other substances. Lead poisoning produces *blue gum* and paralysis of joints specially the wrists. In order to minimise the solubility of lead compounds in weak acids, all lead glazes are required to be fritted before use.

(4). It renders the soluble materials insoluble.

If the soluble matters are left alone, the biscuit wares will absorb some of them and on subsequent firing dense patches may form on those places where the soluble salts get deposited most. Some in-glaze colours are also attacked by the presence of soluble salts in the glaze.

For small quantity of materials, the fritting is done in fireclay crucibles, heated in special furnaces. When the mass smelts completely, it is poured into cold water in order to shatter the vitreous mass. This treatment facilitates grinding. For very heavy charges, reverberatory furnaces, heated with coal, gas or oil, are used. The furnace should be heated before introducing the charge, and the latter when properly smelted, should be frequently stirred with wooden poles, through holes at the side of the furnace, to make the molten mass homogeneous. The heating should be uniform and for lead frits, the atmosphere inside the furnace should not be smoky or reducing; otherwise the lead oxide would be reduced and volatilise. The heating should not be continued too long after the charge has smelted, or loss of alkalies may result.

Those hard glazes which do not contain any soluble material are not fritted, but the raw materials are all ground together to a very fine state, so that no residue is left on a 200 mesh sieve. For small batches, the grinding is done in small *potmills* made of hard porcelain or stone ware cylinders mounted on iron frames

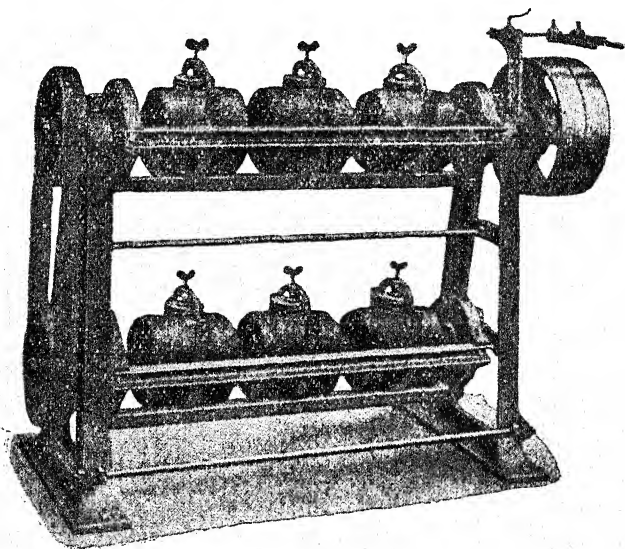


Fig. 15 A set of pot mills.

which rotate slowly; but for large quantities, big *alsing* cylinders or ball mills are used.

After the grinding has been finished, the liquid glaze is passed through an electromagnet to remove iron particles if any; and when whiteness is essential, a little *blue stain* is added to the liquid mass in a very dilute

form. The quality of a glaze improves very much if it is stored for at least a fortnight before use. For this storage, big wooden vats are used provided with a powerful agitator so that the glaze does not settle down at the bottom of the vat. This ageing improves the working property of the glaze to a great extent.

The methods of application of glaze on the clay-wares, vary with different kinds of articles. There are several methods existing in practice of which the following are the most important.

Dipping or immersion. is the most rapid and usually the most satisfactory method of applying an uniform coating of glaze on clay articles. The articles should preferably be in the *biscuit* or baked state, but if in the *green* or unfired state, they should be strong enough as not to lose their shape when moistened with the glaze slip. The thickness of the coating will depend on the porosity of the wares, the time of immersion, and the density of the glaze slip. Glazes for dipping should always contain a little plastic clay or such other plastic materials, to give a binding power to the glaze, when dried on the wares. For this reason, when a glaze is to be fritted, at least a portion of the clay in it, should be kept back and added to the mill mixture before grinding. Sometimes a little gum arabic or dextrin is used for this purpose.

Pouring is employed when the glaze is to be applied on one side of the wares. Hollow vessels whose inside only is to be glazed, are filled with the glaze slip and the excess liquid poured off. Tiles are

sometimes glazed automatically by passing them quickly below a continuously pouring glaze slip so that the upper surfaces of the tiles are coated with a thin layer of glaze.

Spraying, consists in applying the glaze in a form of fine spray by means of a sprayer or *aerograph*, connected to a constant supply of air under pressure of 45-50 lbs per sq. inch.

The glaze should be mixed with a little gum arabic and made up to the consistency of cream and well lawned before use. This method is very helpful for glazing very big articles specially in the green stage, where dipping is very troublesome or sometimes impossible.

Dusting, of very fine glaze powder on green articles which are still damp to retain the powder is now scarcely used except for cheap inferior articles. This process is sometimes applied on some fired articles such as decorative tiles and hand made potteries. A sticky coating is first applied and then the glaze powder dusted carefully over it. This coating or *size* as it is called, is made of organic gums and resins which burn off in firing; leaving no residue to affect the glaze.

Painting, of glazes on wares is done by means of a brush specially on decorative wares, where more than one coloured glazes are required side by side. The glaze liquid is thickened generally by the addition of a little glue or gelatine.

Volatilization, is the process in which the glazing material is put inside the kiln so that it volatilises by the heat of the kiln and gets deposited on the wares. The so called *salt glazing* is the chief process of this nature which will be discussed fully in chapter VI. Zinc in its metallic form is used to produce a variety of green colours on red burning clays by a process similar to salt glazing. These vapour-glaze colours are highly prized specially for face bricks.

Glost Firing. After the application of the glaze, the articles are dried and fired again. This firing is known as the *glost* firing. The pyro-chemical changes that take place during the *glost* firing of a fritted glaze have been studied by Blackey (1938). At 700°C the grains of felspar and quartz are distinctly visible under a microscope. The felspar shows cleavage and some turning, while the quartz shows its concoidal fracture. The other components of the glaze are too fine grained to be recognised clearly.

With the rise of temperature the felspar gets dissolved rather quickly in the molten frit. At 900°C more than three fourth of the felspar goes into solution, and at 1025°C the whole felspar is dissolved.

The rate of solution of quartz in the glassy frit is rather very slow upto 900°C, after which the solubility increases and at 1100°C, whole of the quartz is completely dissolved. At 1145°C the molten glass attacks the body and gradually forms an intermediate layer between the glaze and the body. A good soaking of heat is necessary to develop this layer properly.

The bubbles in the glaze are formed around 900°C when the glaze melts and allows them to take shape. The volume of bubbles gradually increases and shows a maximum at 1025°C after which the volume decreases suddenly. This rapid decrease shows that the glaze is then fluid enough to allow the bubbles to escape.

Glaze faults. Various defects arise during the manufacture of glazed pottery, some of which are seen to disappear before the real cause of their origin could be ascertained; and amongst others the following are the most important.

Crazing and Peeling. As glazes are thin coatings of a kind of glass on the surface of clay wares having different compositions and properties from those of the bodies of the wares, it is not natural to expect them to behave in the same way when affected by heat and cold.

If the contraction of the glaze during cooling is greater than that of the body, the strain or tension thus set up causes the glaze to develop hair like fine cracks throughout the glazed surface of the wares. The greater the antagonism between the body and the glaze, the more numerous are these cracks. This defect of the glazed wares is called *crazing*.

If on the other hand, the contraction of the glaze is less than that of the body the glaze will be under a compression and is likely to detach from the body specially at the edges. The compressive force may sometimes be so great as to break the body into small pieces. This defect, which is opposite to

crazing, is known as *scaling or peeling*. Scaling may also be due to the presence of soluble salts in the body. These salts form scums on the surface specially at the edges of the ware during drying and prevent the glaze to have a grip on the body and cause it to chip off readily.

Glazes like glass take very long time to settle the last contraction after firing, and glazes are often found to craze or peel even after a long period of use. Mat glazes owing to their lower thermal expansion than bright glazes are more resistant to crazing. Blakey (1938) has shown that glazes with slightest tension show an easy tendency to craze while those in high compression show no sign of crazing even after digesting in an autoclave. Autoclaving always moves the glaze stress in the direction of tension because the steam causes the body to expand and bodies with high porosity show a greater tendency to craze.

Tests for Crazing. The common English method is to boil the test pieces for an hour in a saturated solution of common salt and saltpetre, and then to plunge the hot pieces into cold water. If the glaze can stand five such successive treatments, without crazing, it is said to be a fairly good glaze. Certain ceramic bodies expand when treated with water while the glaze remains relatively constant. Hence this wet method is not popular in all countries.

In the American Government method the articles to be tested are heated to an uniform temperature of

175°C for 15 minutes preferably in an electric oven, and quickly plunged into water at approximately 20°C. Development of any craze should constitute failure of the glaze.

Remedies. To remove the defects of crazing and peeling from glaze it is necessary to understand and regulate the co-efficient of expansion of the body and glaze. In older days this could be done only by actual empirical tests but modern researches have made the process more simple. Winklemann and Schott and later Mayer and Havas (1911) have found out the co-efficients of expansion of different oxides which take part in the composition of ceramic glazes, glass and enamels. They have further found out that the final property of the glass or glaze composed of these oxides is *additive* in character. An additive property is one which is dependent not only upon the oxides which the glaze contains but also upon their relative proportions. For instance, if $a+b+c+\dots$ represent the percentage weights of different oxides of a glaze composition and if x, y, z represent the co-efficients of cubical expansion of the oxides respectively then the co-efficient of cubical expansion of the final glaze will be given by the equation:

$$K=ax+by+cz+\dots\dots\dots$$

Winklemann and Schott's factors for the co-efficient of cubical thermal expansion per degree centigrade are as follows :—

Oxides.	Factors in m.m.	Oxides.	Factors.
Na ₂ O	10.0×10^{-7}	Al ₂ O ₃	5.0×10^{-7}
K ₂ O	8.5×10^{-7}	B ₂ O ₃	0.1×10^{-7}
PbO	5.0×10^{-7}	SiO ₂	0.8×10^{-7}
CaO	5.0×10^{-7}	ZnO	1.8×10^{-7}
MgO	0.1×10^{-7}	P ₂ O ₅	2.0×10^{-7}
BaO	3.0×10^{-7}		

Similar values obtained by English and Turner (1931) differ from those given by Winklemann and Schott.

Factors by English and Turner.

Oxides.	Factors.	Oxides.	Factors.
Na ₂ O	12.96	BaO	4.2
K ₂ O	11.7	Al ₂ O ₃	0.42
PbO	3.18	B ₂ O ₃	1.98
CaO	4.89	SiO ₂	0.15
MgO	1.35	ZnO	2.1

As an example for the practical use of these factors we may take the following considerations.

The percentage compositions of a porcelain body and a glaze are given. It is desired to know whether the glaze will suit the body.

Composition of the body. Coef. of expansion.

SiO ₂	$68.3 \times 0.8 = 54.64$
Al ₂ O ₃	$27.0 \times 5 = 135.0$
CaO	$0.3 \times 5 = 1.5$
MgO	$0.5 \times 0.1 = 0.05$
K ₂ O	$3.6 \times 8.5 = 30.6$
<hr/>	
99.7	total 221.79×10^{-7} .

Composition of the glaze Coef. expansion.

$$\text{SiO}_2 \quad 73.24 \times 0.8 = 58.592$$

$$\text{Al}_2\text{O}_3 \quad 15.97 \times 5 = 79.85$$

$$\text{CaO} \quad 3.57 \times 5 = 17.85$$

$$\text{MgO} \quad 0.51 \times 0.1 = 0.051$$

$$\text{K}_2\text{O} \quad 4.81 \times 8.5 = 40.885$$

$$\text{Na}_2\text{O} \quad 1.91 \times 10.0 = 19.1$$

$$216.328 \times 10^{-7}$$

This glaze has a tendency towards compression due to its lower coefficient of expansion than the body. Hence this glaze will stand the test for crazing.

It has been found by experience that a glaze may suit well with a body even though their co-efficients of expansion as calculated theoretically do not tally with each other. This may be due to the elastic property of the glaze and the effects of firing conditions. The knowledge of these values of thermal expansions will indicate whether the glaze is under a strain or compression.

The defects of crazing and peeling can also be cured by following empirical rules.

B. When the glaze is constant.

- (1) Diminish the clay content of the body by increasing the flint. Well calcined flint is more effective than sand or quartz in preventing crazing. Under-calcined flint, in nonvitreous bodies, increase the tendency to craze. Finer grinding of flint or quartz also diminishes

crazing, but over-grinding helps the wares to *dunt* or shatter. With vitreous bodies coarser grinding may cure crazing.

- (2) Substitute ball clay for some china clay in the body. Three or four per cent of lime in a china clay body may produce crazing under conditions when it would not do with a ball clay body. Lime in vitreous body seems to stop crazing to a certain extent. Bone china bodies, which contain lime, craze much less than average earthenware bodies.
- (3) Reduce felspar or fluxes. Both alumina and alkalies in the body favour crazing. If the body vitrifies before any *intermediate zone* is formed between the body and the glaze, the glaze cannot have a firm grip on the body and a little tension may cause them to separate.
- (4) Fire the body harder or for a longer time. Vitreous and porous bodies give opposite results in this respect. Vitreous wares in the first *ring* of the oven may show crazing while those at the second or third ring may be perfect.
- (5) In fire clay bodies, increasing the proportion of *grog* lessens the tendency of crazing.

B. When the body is constant.

- (1) Increase the silica content of the glaze or substitute some silica with boric acid.

- (2) Addition of little china clay or alumina in glaze may cure crazing.
- (3) Substitute the fluxes having low molecular weights (such as potash or soda), with those having high molecular weight (such as lead or barium), as highly alkaline glazes craze more than lead or barium glazes.
- (4) Fire the glaze harder or for a longer time to develop the *intermediate zone*.

For peeling do the reverse of crazing.

Rolling of glazes. When a glaze is softening, in the oven, two different forces seem to act on it. The one tends to keep the glaze fixed to the surface of the body and may be termed, the *adhesive force*. The other, which is due to the surface tension of the melting liquid, tends to help the glaze to crawl away from the free edges of the wares and collect into beads. This force can be termed the *cohesive force*. When the latter force is in excess of the former, the glaze rolls into beads or patches. This fault of the glazes is termed as the *rolling of the glaze*.

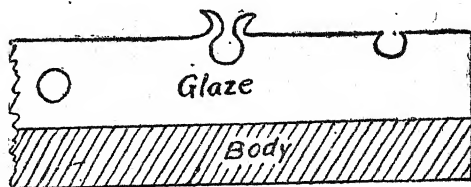
Dusty, greasy, or vitreous surface of the wares lessens the adhesive power of the glaze and help in the rolling of it. Overgrinding of the colours or the glaze, to much earthy colour, or too much magnesia in the glaze, favour the cohesive force and thus help in rolling. Thick dipping and too much china clay in the raw glaze develop fine cracks on the glaze on drying, and if the glaze is not soft enough to heal up these cracks on firing, the glaze will roll into small patches or beads.

Feathering and Sulphuring. Glaze that has been partially crystallised, is more or less covered with dull patches, sometimes with starry or feather-like appearance. Glazes, rich in lime and low in alumina are particularly liable to this defect. The crystals resemble in chemical character wollastonite CaSiO_3 , readily attackable by dilute HCl or HF . Thin glazes can absorb sufficient alumina from the body to retard the formation of crystals. When the top of an oven is chilled with excess air in order to bring up the bottom, this defect is sometimes observed on the wares, formed by sudden cooling.

Sulphates, specially of lime, derived partly from glaze mixture and partly from the fuel gases, are liable to form a thin film on the surface of the glaze which on cooling crystallise and produce dull patches on the glaze.

Feathering is due to crystallisation within the glaze while sulphuring is formed on the surface of it but the nature of the two crystals is quite different. Sulphates are less soluble in more acid glaze; hence as the glaze dissolves some silica from the body and becomes more acid, the dissolved sulphates, come out of the glaze and form a thin film on the surface. If the atmosphere of the oven is made reducing periodically, the sulphates are readily reduced and volatilise, but if the reducing flame does not develop sufficient heat, the acid, formed remains dissolved in the glaze and bursts out later causing other faults.

Pinholes. Small holes are sometimes found on the glazed surfaces of fired wares. These *pinholes*, as they are termed, are generally caused by the evolution of gases, too late to be filled by the fluidity of the melting glazes. Sometimes these holes are formed on the wares during moulding, specially if the moulds are too old or dirty. They disappear during polishing of the wares, just to reappear after firing. If too much dry scraps are used in the casting slip, the small bubbles of air enclosed in the slip, may cause these pinholes during casting of the wares.



Pinholes

Fig. 16 Evolution of Pin holes.

Spitouts. are similar to pinholes in nature but with black specks round them. They are caused by the combustions of carbonaceous matter in solution in the glaze or absorbed by the biscuit wares. If the wares before glazing are stored in a damp ware-house for a long time, the porous wares absorb gases which are forced out during the subsequent glaze firing. The longer the period of absorption, the harder it is to drive out the gases from the wares, and when they are actually expelled, they do so with explosive violence

leaving permanent tracks on the glaze too late to be filled up. Spitouts are frequently found after enamel fire, specially if the atmosphere inside the kiln is too much reducing or smoky. The glaze absorbs the hydrocarbons during the first period of firing and when the kiln gets hotter, these hydrocarbons are expelled leaving small holes with black marks round them.

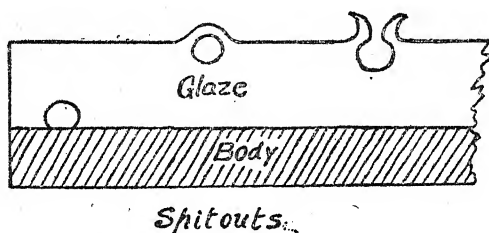


Fig. 17. Evolution of Spitouts,

Ceramic Colours.

Colouring materials used in pottery must be substances that will stand high temperature of firing so it is quite evident that organic colouring matters are useless for this purpose. The pigments generally used for this purpose are either metallic oxides or compounds of such oxides with other substances that modify the colouring properties of the oxides. For example, the same oxide of copper with different materials such as alkalies, borax or lead will produce different colourations. In the following table is given the principal colouring oxides used in ceramic industries and their colouring behaviour with different kinds

of glazes. The conditions of firing such as the oxidising or reducing atmosphere have also great influence on changing the colour of the metallic oxides.

Oxides	High Alkaline Glaze	Glaze with High B_2O_3	High Lead Glaze
CoO	Blue	Blue	Blue
CuO	Blue	Green	Green
Fe_2O_3	Bluish Green	Brown to Yellow	Yellow
MnO_2	Violet	Brown	Yellow to Brown
UO_2	Straw Yellow	Lemon Yellow	Orange
Cr_2O_3	Orange Yellow	Green	Yellow

When individual metallic oxides or their mixtures are used for colouring purpose they are previously calcined at a high temperature. This calcination helps in thorough mixing of the ingredients by so called solution of solids. Double calcination ensures better product. Calcined oxides become less active and produce definite shade during subsequent use at a lower temperature. The high temperature of calcination produces bigger crystals of the colouring oxides which are less active than the smaller crystals. This calcined material is known as *Stain*.

The stain can be used in three different ways. It can be used with the glaze components to produce a

coloured glaze when it is known as *in-glaze* colour. When coloured decorations are made below the glazed surface of the ceramic ware, the colour used for this purpose is known as *under-glaze* colours. When the decoration is to be given upon the glazed surface of the ware, special low-melting colours are used. These are known as over glaze or *enamel colours*.

Underglaze Colours are composed of two distinct parts. (a) The Stain or the real colouring matter and (b) *The flux*. The flux plays the important part of forming an intermediate zone between the body and the colouring matter which ensures the intimate connection between the two different layers. The substance commonly used for this purpose is ground *pitchers*, or ground materials made from the broken wares. A good flux for this purpose can be made by calcining the following materials.

Quartz	45 parts
Felspar	30 „
China Clay	20 „
White lead	5 „

Enamel Colours are also composed of two similar parts but the flux in this case is made from soft glass-forming materials, which help the colouring matters to fuse at the low temperature of the muffle furnace. A portion of it also penetrates the softened glaze and makes an intimate connection between the glaze and the colouring matter.

The following fluxes have got different behaviours with colouring stains and they will be referred afterwards in proper places.

	Flux A.	Flux B.	Flux C.
Red lead ...	3	3·7	2
Borax ...	2	0	2
Silica ...	1	1·3	1

The flux materials are fritted together, ground very fine and kept ready for use. Flux with borax above certain proportion is easily attacked with damp in store houses; the borax goes off first in the form of a white scum which may also attack and destroy the enamel colour.

Preparation of Stains. The mixtures are generally calcinated in small muffle furnaces, but in small factories, they are put in a box made of refractory clay and fired in the same oven with clay wares. There are some difficulties with the latter procedure, as some colours such as chrome green, copper reds, require a reducing atmosphere; whereas others such as pinks, yellows, reds etc require an oxidising atmosphere. The calcined mass is first broken into small pieces and then ground very fine in the same manner as glazes are ground. Grinding of stains should be so fine that no residue should be left on a 250 lawn and finer when necessary. After grinding the stains should be thoroughly washed with clean water. The same stain can be used for making both underglaze or enamel colours by mixing it with different kind of flux in

different proportions, but for underglaze colours it is better to calcine the stain and the flux together to get uniform shade of colour

Cobalt Colours. The pigmentary principle of all blue colours used in ceramic decoration is cobalt oxide, either alone or in association with other oxides. By taking suitable proportions of various ingredients, all shades between deep blue and pale tones can be obtained. Cobalt is generally used in the form of oxides, rarely in the form of carbonate or phosphate.

There are two distinct types of cobalt blue colours. (a). The aluminate or the mat blue, and (b). The silicate or the bright blue. Silica is preferred by cobalt to alumina, so that the silicate blue is easily formed and at high temperature the aluminate is unstable and passes into silicate. Longer soaking in the glost oven destroys the mat colour and changes it into the silicate or bright one.

Mat blue colours are prepared by calcining the following ingredients together, to about Seger cones 3 or 4 and then grinding and washing the calcined mass.

The alumina is prepared by calcining equal parts of potash and ammonia alums and then thoroughly washing the mass to get rid of the potash sulphate formed.

Some blue stains :—

	1	2	3	4	5
Cobalt oxide black ...	5	5	10	20	10
Calcined alumina ...	5	90	60	60	10
Zinc Oxide ...	90	5	30	20	80

1. Pale Green. 2. Sky blue. 3. Light blue. 4. Royal blue. 5. Greenish blue.

Chinese blue can be imitated by adding very small amount of manganese dioxide which imparts the delicate shade.

Since leadless glazes contain more alumina than lead glazes, mat blue is more stable in the former than in the latter.

Silicate or bright blue colours are known by various names; marine, ultra-marine, mazarine, willow, canton, sable etc. They are prepared by calcining the mass at about cone 9 for the underglaze blue but at lower temperature for enamel colour.

Following are some bright blue recipes.

	1	2	3	4	5
Cobalt oxide black...	50	45	—	—	15
Barytes	5	—	—	—	10
Whiting	45	—	—	—	—
Zinc oxide	—	—	20	40	75
Ball clay... ..	—	55	50	50	—
Cobalt phosphate ...	—	—	30	10	—

1. Mazarine blue for banding. 2. Dark blue for all purposes. 3. Medium blue. 4. Marine blue. 5. Turquoise blue.

Body Stain. It has been already mentioned that in order to make milky-white bodies, a little blue stain is generally mixed with the mass. The amount of cobalt oxide required for this purpose is so small that, it is quite a difficult task to mix the oxide with the body

uniformly. To avoid this difficulty, the oxide is diluted with some inert materials such as flint and stones, in order to reduce its colouring power and avoid the possibility of blue specking on the wares.

Soluble cobalt salts are sometimes used for this purpose and the cobalt is precipitated in the clay mass by the addition of a little amount of ammonia.

A good body stain can be prepared by calcining the following ingredients at temperature of cone 3 or 4.

Ball Clay	...	50	—
Cobalt oxide	...	35	25
Flint or quartz...	—	12	
Felspar	...	—	8
China clay	...	10	5
Whiting	...	5	—

Grind wash and lawn through 200 mesh sieve before use. 0.1 to 0.3 per cent of this stain is enough for ordinary purpose.

Flowblue. In a certain type of decoration the blue colour is made to flow during firing of the ware. This is done by generating chlorine gas inside the saggars by heating lead chloride or similar substances. The chlorine is partly absorbed by the glaze and partly by the cobalt stain forming soluble cobalt chloride. At higher temperature the gas absorbed by the glaze escapes and the cobalt salt flows through the tracks left by the gas. The flow powder is kept in a pot and placed inside the saggars with the decorated wares so that the vapours evolved from the flow powder can distribute themselves evenly round the wares. The

blue stains used for this purpose should be so prepared that they can be easily attacked by the vapours and rendered into soluble salts.

Some flowblue recipes :—

		(1)	(2)	(3)
Cobalt oxide	65	55	50
Silica powder	10	25	30
Nitre	2·5	—	20
Red Lead	10·5	4	—
Borax crystals...	...	12	6	—
Felspar	—	6	—
Whiting	—	4	—

The calcination of the stains need not be so hard as ordinary blues.

Flow powder.

White lead ...	38
Common salt ...	18
Borax crystal ...	14
Whiting ...	30

Mix the whiting and the white lead together and stir with HCl so long as effervescence occurs. Then mix with the mass the borax and salt thoroughly.

Defects in blue decorations.

Milkiness. It is often observed that glazes containing blue stains show after the glost firing a milky opalescence very similar to the scumming fault. This milkiness in the glaze is due to incipient crystallisation in the glaze. Cobalt stimulates this crystallisation process. Very slow cooling of glost

oven gives this milkiness. The crystals grow best when the glaze has just congealed, between liquid and viscous stage.

These crystals are due to the formation of calcium monosilicate $\text{CaO} \cdot \text{SiO}_2$ and are formed when the glaze contains high lime and low lead oxide or alumina. When cobalt blue show milkiness, strike out the whiting from the formula and add alumina, as it retards crystallisation. The limit of alumina is 12 per cent, above which the tint suffers and there is danger of mat effect.

Ironing. This is due to little flux or too much cobalt. The flux gets saturated with cobalt and some of the latter separate out in cooling as reddish or pinkish patches known as ironing of blues. When this happens paint over the patches with red lead and refire. To alter the colour recipe, increase the flux or decrease the cobalt. If too much of flux is added the colour may flow. Magnesia in body, glaze or stain, also tends to change the cobalt blue into purple.

Spattering. In this defect the coloured surface gets broken up into several patches specially when any size or *ground laying oil* is used. Biscuit and glazed wares get damp when kept in a moist place for a long time and when oil is brushed over them for decoration purposes, the moisture get entrapped in the impermeable oil coating and force their ways through the colour film when fired in the glost or muffle ovens.

Steaming. If the coal used for firing contains sulphur, the sulphur gases with steam produce H_2SO_4 which

attacks the iron compounds of the saggar rendering them soluble. The solution of iron sulphate then drops on the wares. The acid also attacks the glaze and decoration causing the latter to flow in some cases. When this trouble occurs it is advisable to use coke in the first part of firing and avoid the generation of steam and hydrocarbons. At higher temperature coal can be used and steam generated from coal is driven away easily.

Spitting. This defect occurs on blue bands. It is mainly due to the use of too much heavy oil in painting. Carbon in the oil gets skinned over and trapped under the soft enamel flux and on further heating air gets into the carbon which burns out with explosion, not slow combustion as at low temperature.

Specking. If the stain is not properly calcined and if the glaze contains high amount of raw whiting, the fusible frit covers up the CaCO_3 and does not allow it to decompose easily. At higher temperature CO_2 gas blows out forming blisters. When the temperature is raised further up these blisters are healed up but leave black specks with a white halo round them. Cobalt and manganese stains particularly show this weakness. In such cases calcine the stain harder and use more china clay in the mill to keep the glaze open for a longer period. Avoid whiting in the mill.

Copper colours. Copper oxide gives different colour with different kinds of glazes. In ordinary glaze it gives green colour which is very simple to make by fritting the oxide and the flux together at temperature

not above 1000°C, as copper begins to volatilise at higher temperature and for this reason this colour is unsuitable for underglaze decoration. A good enamel green colour can be made by fritting together the following ingredients :—

Copper oxide	...	10
Flint	...	25
Red lead	...	60
Borax	...	5

In highly alkaline glazes copper produces a very pleasant blue colour generally known as *Turquoise blue* which has a great tendency to turn down into green. Pure alkali silicates dissolve copper oxide forming a deep blue colour but when part of the silica is replaced by boric oxide the greenish shade developes. The presence of Al_2O_3 favours the passage of blue into green. If part of the alkalies is replaced by lime, baryta or magnesia the tint changes into green, but alkali-lead silicates remain blue so long the lead does not exceed the alkalies. In this case potash-lead silicates are more stable than soda-lead ones. Hence turquoise blues from copper are alkali-lead silicates with very narrow limits for variations. A good turquoise blue enamel can be made from the following formula :

Sand or flint...	...	47.15
Red lead	...	23.58
Sodium nitrate	...	11.80
Potash nitrate	...	12.76
Copper oxide	...	4.71

Atmospheric moisture is liable to attack the high alkali and destroy the colour. To make the glaze the copper oxide should be added in the mill and not in the frit. These glazes are very liable to craze.

In reducing atmosphere copper yields red colours. There are two types of copper reds ; (a) in glaze reds or *rouge flambe*, and (b) on glaze reds or *copper lustres*. Both these colours are very difficult to make. A good copper lustre can be made from the following formulas:—

	<i>Arabian lustre.</i>	<i>Italian lustre.</i>
Copper sulphide ...	26·87	24·74
Silver sulphide...	1·15	1·03
Mercury sulphide ...	—	24·74
Red earth ...	71·98	49·49

The ingredients are well mixed with a little gum tragacanth, and the paste painted carefully on the glazed surface with a brush. The dried pieces are then fired in a muffle oven under strongly reducing atmosphere and at a temperature not high enough to make the red earth stick to the glaze. Sawdust or pieces of wood are generally introduced into the oven when it is hot enough, in order to keep the atmosphere reducing.

The presence of a small amount of silver softens the copper and imparts a bluish tinge to the red. A small amount of bismuth developes a very beautiful mother-of-pearl iridescence.

A few formulas for red lustres :—

Copper Carbonate ...	80	30	28	15	—
Silver carbonate ...	5	—	2	3	1
Bismuth nitrate ...	—	—	—	12	10
Copper oxalate ...	—	—	—		5
Red earth or ochre...	15	70	70	70	84

After firing clean the surface of the wares with a hard brush.

Iron Colours. Iron oxides produce a variety of colours ranging from reddish yellow to brown. Under reducing conditions similar to copper reds, iron gives *Celadon green* colour which was so favourite to the Chinese.

Iron oxide used for making potter's colours is made by calcining crystals of ferrous sulphate. Just above 500°C the crystals break down into fine powder of Fe_2O_3 a yellowish red colour. If zinc sulphate or alumina is mixed with the iron salt the yellow tint is much intensified, finally turning to orange or brown. By raising the temperature of calcination to about 600° to 650°C, coral red or blood reds are obtained, and by further heating to about 700-750°C, violet brown or violet blacks are obtained. Presence of MnSO_4 intensifies the blackening of the tint. It is believed that the grain size of the particles causes the difference in shades of colours. The higher the temperature of calcination, the larger are the sizes of the particles and deeper are the shades produced.

Preparation of red oxide. Finely pulverise pure green vitriol and gently heat the powder to expell the water of crystallisation but do not melt it. The white anhydrous powder is again pulverised, the finer this is done, the purer will be the colour. It is then placed in thin layers in a muffle, which is slowly raised to red heat. As soon as the desired shade is obtained, (600° - 700° C) the muffle is allowed to cool slowly. The cold mass is repeatedly washed with boiling water to remove the undecomposed sulphate, which gives afterwards efflorescence of small white specks on the colour.

The reds from iron are best produced as over glaze colours as iron reds do not stand high temperature. High lead flux is more favourable to produce the red than high borax flux. The oxide should be ground up very finely with 3 to 4 times its weight of the flux. Pannetier, who acquired the greatest reputation in making iron reds advocated the use of a flux composed of—Red lead 12 parts, flint 4 parts, and borax 3 parts. His shades comprised of eleven tints ranging from orange to grey.

All the tints which the oxide assumes varying from orange to violet can be decomposed into yellow, red and blue. The lower the temperature the more is the colour inclined to yellow and the higher the temperature the more is it inclined to blue. The tint will be purest when the oxide is formed from identical molecules. The tint will be of perfect purity when

all the molecules have been heated uniformly to the temperature necessary for the development of the colour.

Analyses of Pannetier's Iron colours.

Names	Silica	Lead ox	Borax	Iron ox	MnO ₂	Alumina	ZnO.
Orange Red	17.48	51.54	13.08	14.10	—	trace	3.8
Nasturtium Red	16.60	50.39	12.51	20.50	—	„	—
Blood Red	16.90	46.51	13.39	19.70	—	0.40	—
Flesh Red	16.60	49.18	14.22	20.00	—	trace	—
Carmine Red	16.30	50.02	13.68	20.00	—	„	—
Red lake	16.40	49.44	15.96	18.20	—	„	—
Pale Violet Red	16.85	50.66	12.66	18.83	—	„	—
Violet Red	16.39	50.52	12.01	21.08	—	„	—
Deep Violet Red	16.56	50.09	15.36	17.99	—	„	—
Very deep Violet Red	16.40	50.60	12.14	18.71	2.15	„	—
Iron Grey	15.55	43.05	15.48	18.60	—	„	—

Natural iron minerals are not suitable for yellow or red colours at high temperatures except Thivier's

earth which alone can stand high temperature without breaking down. This mineral sometimes called Japanese red, is calcined and used for colouring *Semian bodies*. About 5 per cent of this earth mixed in the body gives a very handsome flesh tint after firing.

A typical composition of this mineral is as follows, but it often varies to a great extent.

Fe_2O_3	8.24
SiO_2	87.38
Al_2O_3	1.25
Loss	1.20

A red stain for painting can be obtained by fusing together 80 parts of Thivier's earth and 20 parts of red lead, and grinding the fused mass very finely. Artificial Thivier's earth can be prepared by mixing a solution of aluminium sulphate with one of ferric sulphate in proportions furnishing the above ratio between the two oxides, and then treating the liquid with a solution of water-glass so long as a precipitate continues to form. This is carefully washed, dried and strongly calcined.

Increasing the amount of ferric sulphate in the liquid deepens the colour of the resulting red ; and conversely a lighter shade is obtained by increasing the proportion of the alumina. This red may be used as an underglaze colour, but not under a strongly acid glaze, or the compound will be attacked by the silica or boric acid present in the glaze and a yellow colour being then obtained owing to the formation of ferric silicate or ferric borate.

Manganese Colours. Under glaze colours of both very deep and light brown shades can be produced by using manganese compounds. True manganese brown consists of a mixture of manganous oxide and alumina. It can be obtained by mixing solutions of manganous sulphate and potash alum, and treating the liquid with a solution of sodium carbonate, so long as a precipitate continues to form. The precipitate is then washed, dried and calcined. The proportions of first two solutions determine the shade of the colour produced. This stain is mixed with fluxes and used as colours.

The chief natural ore of Mn used for this purpose is *Pyrolucite* which may vary in composition within the following limits.

MnO ₂	...	70-95	per cent
SiO ₂	...	0-2	" "
Al ₂ O ₃	...	0-1	" "
Fe ₂ O ₃	...	0-5	" "
CaO	...	0-1	" "
Loss	...	1-5	" "

Stains from pyrolucite can be prepared from the following mixtures.

Pyrolucite	...	20	25
Alumina	...	80	—
Felspar	...	0	75

Manganese phosphate is sometimes used to produce violet brown stains.

Manganese phosphate... 70 parts.

Tin oxide 30 „

Calcine the mixture hard. Best browns are obtained from mixed oxides.

In highly alkaline glazes or fluxes, manganese produces violet colours due to the formation of permanganate of alkalies. The amount of MnO_2 required varies from 0.5 to 2 per cent according to the shade required.

Glazes containing high manganese dioxide have tendency to blister or produce dull brownish patches. When MnO_2 is calcined, it may take up the form Mn_3O_4 or Mn_2O_3 but when these oxides dissolve in glazes they break down to MnO which produces the characteristic brown colouration of manganese glazes. The liberated oxygen may produce blisters or pinholes in the glaze specially if the stain is calcined at a higher temperature, because hardly calcined oxides dissolve but very slowly in the glaze. The undissolved oxides produce dull patches in the glaze. The solubility of MnO in normal glazes is not very high. So if added in excess, it comes out of the glaze to form dull patches.

Uranium Colours. This metal produces a series of yellow colours ranging from pale green-yellow to bright scarlet in an oxidising fire and a dirty greenish brown to deep black in a reducing atmosphere. The colours are stable and can be used when other yellow colours generally break down. The so called dark

orange oxide sold in the market and generally used for making this colour is a potash or soda uranate,— $\text{Na}_2\text{O} \cdot 2\text{UO}_3$.

Uranium gives a deep orange shade to glazes rich in lead. The best lemon or yellow colours are obtained in glazes high in alkali and low in lead. About 5 per cent of the oxide in an ordinary earthenware glaze gives very satisfactory results. If more than 10 per cent oxide is used the excess separates out as a dirty scum when the glaze cools down. In porcelain about 8 per cent of yellow oxide produce deep black, in reducing fire.

Good enamel colours are obtained by mixing the so called yellow oxide, with 3 to 4 times its weight of either flux A or B. With the former flux yellow shades are obtained while with the other, orange or lemon colours are made.

An idea of different shades produced from different glazes can be obtained from the following results.

Glaze composition.	Uranium oxide. Shade. Per cent.
(1). 1.0 PbO . 0.15 Al_2O_3 . 1.7 SiO_2	4.5 Deep Orange
(2). 0.75 PbO .	
0.14 K_2O . 0.15 Al_2O_3 . 1.7 SiO_2	3.0 Bright Orange-
0.11 CaO .	yellow.
(3). 0.35 PbO .	
0.35 K_2O . 0.15 Al_2O_3 . 1.7 SiO_2	3.0 Bright Lemon-
0.30 CaO .	yellow,

Mixtures of Uranium oxide with 20 to 40 per cent iron oxide produce various shades of orange reds.

With cobalt oxide and Uranium oxide the whole range of *Jade green* colours are obtained.

Chromium Colours. This metal produces various shades of colours like green, yellow, orange and pink in different compositions of glazes and under different conditions of firing. Chrome-greens require strong reducing condition while yellows, oranges and pinks are best produced under strong oxidising atmosphere.

All chrome greens require good washing after calcination. Better results are obtained by mixing some sawdust with the colour mixture during calcination to keep the atmosphere reducing. Whiting, when mixed with Cr_2O_3 produces victoria green or emerald green

English. German.

Potash dichromate ...	38	36
Whiting	20	20
Fluorspar... ..	20	12
Flint	22	20
Calcium chloride ...	—	12

Fluorspar (CaF_2), calcium chloride, or old plaster moulds, seem to make the green colours more stable and give brightness. ZnO , when mixed with chrome oxide, makes the colour brown.

Glazes high in lime and lead are most favourable for this colour. Leadless glazes high in alumina are

not suitable for the purpose because chromic oxide does not dissolve in such glazes, and makes the glazes dull.

Lead chromate or chrome yellow produces yellow colour in glazes and enamels high in lead. Good enamel yellow colours can be produced by fusing at about 600°C the following mixtures,

Red lead	70	80	40
Lead chromate,	...	10	—	30	
Chromic oxide	...	—	5	—	
Borax	12	10	20
Quartz	8	5	10

For yellow glazes 10-15 per cent of lead chromate is used in high lead glazes fired under oxidising condition.

Coral Reds can be prepared by fritting together 35 parts of lead chromate and 65 parts of red lead, with three times its weight of flux A. These coral reds are distinguished by the brightness of their colour. These reds should be fired at as low a temperature as practicable and as quickly as possible. If the temperature is too high, the colour breaks down. In firing coral reds, the atmosphere should be oxidising with good ventilation inside the kiln, as reducing condition gives dirty green effect.

Chrome pinks. The pink and deep crimson colours are obtained by calcining at temperature 1200-1300°C under strongly oxidising conditions, three parts of

tin oxide SnO_2 and 1-2 parts of lime CaO , with 1.5 per cent of a chromium salt. A small amount of SiO_2 brightens the colour but larger amount impoverishes it. Substitution of part of the lime with CaF_2 improves the pink. Thorough washing of the calcine is essential. If the calcine is not bright, grind well and recalcine it.

Chromic oxide in an extremely fine state of subdivision appears to be crimson. There is some evidence to show that the red colour is not due to the formation of a chemical compound and that the chrome-tin colour is related to purple of Cassius. A chrome alumina colour can be prepared which appears green in daylight or in reflected light and crimson in transmitted light or in artificial light, thus resembling the mineral 'alexandrite'.

Tin oxide acts as a 'mordant' by helping a very thin film of chromic oxide to fix on it but itself remaining unaffected. If the proportion of Cr_2O_3 is greater, it will react with the lime and develop a green shade.

In reducing atmosphere SnO_2 will be reduced to metallic tin and volatilise. A high temperature and sufficient time are essential to obtain a rich dark red colour.

In actual practice it is found that the same chemical composition yields different depths of pink with different raw materials used. The following are a few compositions of chrome pinks and reds.

CaO	PbO	K ₂ O	SnO ₂	Cr ₂ O ₃	SiO ₂	Remarks.
63.11	—	20.68	151	3.31	26.22	Blood Red.
112	12.93	—	151	4.40	200	Bright Red.
49.72	6.91	—	151	2.35	60	Intense Red.
48.4	2.9	7.9	151	10	58.6	Pink.

Calcine at cone 10-12 and wash well.

A few typical recipes are given below.

	1	2	3	4
Lead chromate ...	9.35	—	—	—
Chromic oxide ...	—	4.4	—	—
Potash bichromate	—	—	5	1.5
Red lead	6.63	13.1	—	—
Tin oxide	151.0	151.0	60	160
Quartz	202.0	202.0	5	64
Whiting	200.0	200.0	30	64
Calcium chloride	—	—	—	15
Soda Nitre ...	—	—	—	16

1. Pink. 2, Dark pink. 3. Rose. 4. Rose-du-Bari.

Dissolve the bi-chromate in water and mix thoroughly with other ingredients and then calcine the mass very hard under oxidising atmosphere at cone 12.

Powder the calcined mass and wash it thoroughly in warm water till the wash water is clear. These stains can be used for underglaze or inglaze colour but for enamel purpose, mix 3 to 4 times its weight of flux A.

With high lime glaze use less whiting and vice versa. Leadless glaze breaks the colour, so use lead chromate in the recipe. Glazes high in alkali dissolve some of the tin oxide and impoverish the tint.

An ordinary majolica glaze contains rather too much of silica and too little of lime for a first class crimson colour and a better result is obtained with a glaze of the following type.

0.5 PbO		1.1 SiO ₂
0.3 CaO	0.08 Al ₂ O ₃	0.3 B ₂ O ₃
0.2 alkalis		

A portion of the glaze can be fritted with the colour, 5-15 per cent according to the tint required.

Sometimes chrome pinks turn purple after the glaze firing, specially if the temperature of firing is high. In such cases add more tin oxide in the stain recipe. If a small quantity of chromium is added in the glaze recipe, it gets dissolved in the glaze and produces a yellow glass in which the red coloured particles are suspended, so that the violet of the purple colour is neutralised by the yellow.

Influences of raw materials on the pink colour.

Lime favours the development and stability of the colour. With decreasing proportions of lime in the

recipe the colour is liable to turn to purple, and brown. Pink stains with low lime content often breakdown in the glaze firing at high temperature. If the lime content is more than 25 per cent the tints become weaker. Strong and stable stains are generally made with three parts of tin oxide and two parts of lime. Substituting the lime with calcium fluoride or old plaster would deepen the tint. Bone ash makes the colour unstable.

Silica. Introduction of a small amount of flint in a standard recipe brightens the colour and makes it more inclined to pink but more flint impoverishes the colour. But, if the deficient tin oxide is added to the glaze mixture the colour is restored.

Boric acid. A small proportion up to 3 per cent, makes very little difference but a higher proportion makes the colour liable to turn purple or brown.

Alumina. Addition of Al_2O_3 makes the colour less stable, but the addition of a little china clay to the under glaze colour helps it to adapt itself to the glaze.

Antimony colour. Antimony acts as an acid like SiO_2 and B_2O_3 forming compounds with other metallic oxides. The alkali antimonates are white compounds largely used in white glazes and enamels. Sodium antimonate is sold as *Leukonin* in trade and used as an opacifier. The only colour made from antimony is lead antimonate $\text{Pb}_3(\text{SbO}_4)_2$ a yellow colour known in trade as *Naples Yellow*. The tint of this colour depends upon the proportions of the ingredients and the temperature of heating. The shade can be modified by using a small proportion of iron oxide.

	1	2	3	4
Red lead	60	45	40	45
Antimonyoxide ...	40	50	40	30
Soda Ash	--	5	12	—
Iron oxide... ..	—	—	8	25

1. Pure Naples yellow. 2. Light yellow. 3 Deep yellow. 4. Dark yellow.

Calcine the mixtures at 950°C under strongly oxidising conditions. These yellows are best used as enamel colours with 4 times of flux. As in-glaze or under-glaze colour they are unreliable.

Cadmium colour. The yellow CdS is often used in enamels and glazes free of lead, as the presence of lead darkens the colour of the glaze due to the formation of lead sulphide. It is prepared by passing H_2S into a solution of cadmium salt, chloride or sulphate.

For colouring glazes and enamels 1 per cent of this salt is quite good. It is generally added in the mill batch. If fritted the frit becomes white when quenched in cold water. The colour reappears after the glaze or enamel is fired again. The CdS is supposed to dissolve in the frit, but separates out again in finely divided condition when the glaze is fired again.

Gold colours. Pink and red colours are often made from gold besides metallic gold lustres. By adding a solution of gold chloride AuCl_3 to a mixed solution of the two tin chlorides, a precipitate can be obtained varying in colour from violet blue to purple, red, green, yellow and brown, according to the concentration of

the different solutions, as well as the temperature and nature of the substances present.

Stannic chloride alone gives no precipitate with AuCl_3 . Stannous chloride gives a brown or yellowish brown precipitate. A mixture of the two is necessary for the purple and red. If SnCl_4 is in excess the colour is inclined to be yellow, like gold itself, and if in great excess, blue or green. An excess of AuCl_3 solution in the cold does not make much difference to the tint but if the solution is warm the colour may be violet, chestnut brown or red.

It is believed gold chloride is reduced to fine metallic gold by the stannous chloride while the stannic chloride acts as a mordant for the gold to deposit on it. If other substances as alumina, baryta etc. are used for the mordant they are dissolved in the glaze under the pottery conditions.

If ammonium-stannous chloride is used in place of SnCl_2 , the operation can be controlled better.

Gold purple can be prepared in the following way. Dissolve separately 1 part of stannous chloride- SnCl_2 and 2 parts of stannic chloride- SnCl_4 , and mix the two solutions into a very dilute solution of 1 part of gold trichloride AuCl_3 . A purple precipitate is formed which gradually subsides. Alcohol helps deposition. This is known as *Cassius Purple*. The gold chloride should be free from nitric acid and as much neutral as possible. The purple will be finer in colour in proportion to the degree of dilution of the solutions used. The precipitate is ground up with silver chloride, and ignited at red.

heat. Too much silver turns the tint from pink to purple. If the colour is underfired, it will have a brownish tint, if overfired purple.

Gold colours are very sensitive to temperature and hence sometimes used as pyroscopes in the muffle kiln.

Gold colours best develop in glazes and enamels containing lead and potash, and fired under oxidising conditions.

Ruby red glass or enamel can be obtained from the following mixtures:—

Pure Quartz Powder	37	30
Red lead	48	40
Potash nitrate	6	5
Potash carbonate	9	5
Borax powder	—	18
Tin oxide	—	2

For ten thousand parts of the batch add one to three parts of pure gold chloride in very dilute solution. Thorough mixing is necessary before fritting. The fritting must be hard. It is often found that after cooling, the glass is either colourless or of straw yellow colour but on reheating the red again appears.

Platinum colour. This costly metal is sometimes used to produce grey colours stable at all temperatures. The stain can be prepared in the following way.

Dissolve fine chippings of the metal in a freshly prepared mixture of one part of strong nitric acid and three parts of strong hydrochloric acid, on a water bath. Evaporate the solution of platinum chloride to dryness

and then add to it an equal quantity of ammonium chloride dissolved in water, the whole being evaporated to dryness again. The product is then dissolved in water and soaked in powdered biscuit porcelain, dried and calcined. The amount of platinum used determines the strength of the grey. For enamel colour any soft flux can be used.

Mixed Colours. A large number of shades of colour can be obtained from mixed oxides. Calcine the mixture at 1160°C , grind and wash well. 3 to 5 per cent of the stains in a glaze or enamel produce good colours.

	1	2	3	4	5	6	7	8
Ferric oxide. ...	30	20	10	40	—	—	—	12
Chromic oxide. ...	20	30	40	10	40	50	—	10
Cobalt oxide. ...	—	—	—	—	10	—	10	—
Manganese oxide. ...	—	—	—	—	—	—	16	—
Zinc oxide. ...	20	30	40	40	—	—	32	50
Felspar. ...	—	—	—	—	25	—	24	—
Gypsum. ...	—	—	—	—	10	—	—	—
Kaolin. ...	30	20	10	10	15	50	18	28

1. Deep chocolate. 2. Deep chocolate—brown.
 3. Greenish brown. 4. Deep brown. 5. Grass green. 6. Deep green. 7. Violet. 8. Salmon.

Kaolin, calcined previously at $850\text{--}900^{\circ}\text{C}$ produces more stable stains. The gypsum may be replaced by old plaster moulds with advantage.

The following are some recipes of lighter shades of colours.

			1	2	3	4	5
Tin oxide.	66	65	—	50	—	
Borax.	30	25	—	—	10	
Potash dichromate.	4	—	35	10	—	
Kaolin.	—	6.5	35	10	8	
Lead chromate.	—	3.0	—	—	25	
Cobalt oxide.	—	0.5	—	—	—	
Zinc oxide.	—	—	15	25	50	
Iron oxide.	—	—	15	5	7	

1. Lilac. 2. Violet. 3. Claret brown. 4. Orange.
5. Blood red.

Greys and blacks can be obtained from the following mixtures calcined at 1160°C.

			1	2	3	4
Ferric chromate.	95	90	75	70	
Cobalt oxide.	—	5	—	15	
Manganese dioxide.	5	5	25	15	

1 and 2 are greys, while 3 and 4 are jet blacks. Use 10 per cent in glazes and enamels.

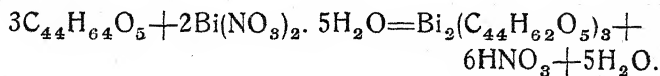
Metallic Lustre. When a very thin coating of a metal is imparted on a glazed pottery, the surface of the ware acquires a peculiar sheen which is not inherent in the glaze. Light incident on the very fine coating of metal is refracted and produces iridescent effect peculiar to the metal selected. Thus, bismuth, aluminium, lead and zinc produce the mother-of-pearl or moon shine effect, while uranium, copper, iron, nickel, cadmium, and cobalt produce different coloured effects.

Combination of two or more metals produce very satisfactory results.

The ancient Arabs and Italians were well versed in the production of this type of artistic ware and their methods of producing copper lustre has already been discussed in previous pages.

The modern practice of producing lustre is by the wet process, the products used being known as *Liquid lustres*. In composition these liquid lustres are chemical compounds of metals with pine resin or colophony, dissolved in suitable solvents. These lustres are applied on the wares by means of a brush and fired in muffle ovens. Uniformity of application plays very important part on the nature of the lustre effect. After brushing the lustre liquid the wares are to be dried quickly, otherwise the oily liquid collects in small drops making the surface uneven.

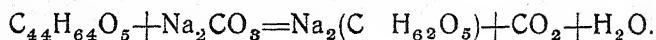
Bismuth, zinc and lead lustres are prepared by the dry process.



Take 25 grams of rosin and melt over a low fire. Then add gradually in the molten rosin 10 grams of finely powdered bismuth nitrate or 7 grams of bismuth subnitrate stirring the melt well all the time till the mass becomes brown. Then add to the mass 75 c. c. of spike lavender oil and stir well again till the mass is dissolved in the oil. Remove it from the fire and leave aside for 24 hours to allow the undissolved

portion to settle down. Decant off the clear liquid in a stoppered bottle for use. The undissolved residue can be used over again with fresh mixture. If the clear liquid is too thin for proper application it can be thickened by placing a small amount on a porcelain dish and exposing it for some time in air before application with a brush. Zinc and lead lustres are prepared in the same method using acetates of the metals. Use one part acetate with three parts of rosin. Use 7 parts of turpentine oil for 4 parts of the resinates. Aluminium lustre can be made both by the dry or wet methods.

Lustres from uranium, copper, cobalt, iron etc. are made by the wet process. In this process an alkali rosin soap is first prepared.



Dissolve 20 grams of soda ash in 150 c. c. of water and boil. Add to this boiling liquid 100 grams of finely powdered rosin in small amount and with constant stirring. Each addition should be made after the frothing subsides. Towards the end when all reactions subside, add 100 c.c. more water to dilute the thick rosin soap formed. Keep aside for 2 to 3 days to allow the uncombined matter to settle down. Decant off the clear liquid in another vessel for use.

To prepare the metallic resinate, take very dilute solution of a salt of the respective metal and add it drop by drop into the solution of the rosin soap when a thick precipitate of the resinate of the metal will be

formed. Filter the precipitate, wash with hot water, dry and keep in a stoppered bottle. It is better to keep these resinate powders in coloured bottles as some of the resins become insoluble when exposed to strong light for a long time. These resins require special solvents, some of which are given below.

Uranium Lustre.

Uranium resinate	6 gms.
Oil of turpentine	5 c.c.
Toluol	10 c.c.

Iron Lustre.

Iron resinate ...	7 gms.
Oil of turpentine	5 c.c.
Toluol... ..	10 c.c.

Copper lustre.

Copper resinate	5 gms.
Toluol	10 c.c.

Cobalt lustre.

Cobalt resinate	15 gms.
Spike lavender	80 c.c.
Terpentine ...	5 c.c.

Mixed Lustres. As different metals used for this purpose soften at widely different temperatures, it is necessary to bring the melting points of these lustres to a suitable temperature, consistent with other decorations. This is adjusted by mixing more fusible metals with those of higher melting points. The following lustres are adjusted to a temperature of cone 0·18 in a muffle furnace. When the lustre is applied on glazed pottery and dried, the volatile oils evaporate, and there remains a coating of the resinate of the metals. On firing the ware the resins decompose leaving behind on the surface of the glazed ware an exceedingly fine layer of the metals which readily stick to the glaze owing to the low temperature of fusion of the alloy. The effect

of light on this thin metallic surface coating produces the peculiar sheen which cannot be produced by any other means.

(1) *Lemon yellow lustre.*

Uranium lustre ... 4

Bismuth lustre ... 1

(2) *Orange lustre.*

Iron lustre ... 3

Bismuth lustre 1

Lead Lustre ... 1

(3) *Golden lustre.*

Uranium lustre... 2

Iron lustre ... 2

Bismuth lustre... 1

(4) *Steel grey lustre.*

Cobalt Lustre... 3

Lead lustre ... 1

Bismuth lustre... 1

(5) *Bronze lustre.*

Cobalt lustre ... 1

Iron lustre ... 2

Lead lustre ... 2

(6) *Mother-o-pearl lustre.*

Bismuth lustre... 2

Tin lustre ... 1

Aluminium lustre 2

Tin lustre is prepared in a different method.

Warm 10 parts of sulphur balsam on a water bath and slowly add to it with constant stirring 3.5 parts of stannous chloride. When the tin salt has practically dissolved in the viscous liquid, add to it 22 parts of a solution of lavender oil 6 parts, oil of clove 3 parts, and nitrobenzene 1 part. Stir well till the liquid is homogeneous and thin. The solution is then left to stand for some time till the undissolved matter settles down. Sulphur balsam may be prepared from the following formula.

Larch terpentine	14	15	33
Flower of Sulphur	14	10	8
Oil of terpentine	72	75	59

Mix the larch terpentine with half the amount of the oil of terps by gentle heating. Add the flower of sulphur and heat till the sulphur melts to a clear brown liquid. Stir well the two liquids for some time till a black homogeneous mass is formed and brown fumes begin to come off. Add the remaining oil of terps and stir well. The cooled mass should show a clear black liquid. Any turbidity or precipitate after the liquid has stood for sometime show that all sulphur is not dissolved. In such cases heat again with stirring.

Liquid Gold. This preparation is a resinous liquid which when applied on a glazed pottery or enamelled ware dries up quickly and when fired in a muffle oven leaves a bright metallic gold coating on the surface of the ware. It is prepared by either dissolving gold in sulphur balsam or keeping it in suspension in a very fine colloidal condition. The exact nature of this preparation is not well understood. It is believed that gold is converted into a gold-terpen-sulphide which readily dissolves in essential oils. As gold has a high melting point, it is necessary to use small proportions of tin, bismuth or uranium, with it so that the gold softens at a lower temperature and adheres better to the ware after the muffle fire. Gold is a soft metal. Hence the gold decoration will wear out sooner unless it is hardened. For this purpose, a very small amount of rhodium or chromium may be used which will prevent the gold to wear off easily. Sometimes iron and uranium are also used in order to lower the percentage of gold used in the preparation. Generally 10 to 12 per

cent. of pure gold is used for the preparation of liquid gold.

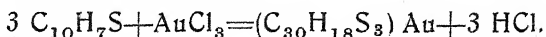
Gold chloride AuCl_3 is generally used for this preparation. It can be prepared by dissolving pure gold in *Aqua Regia*. The gold chloride must be free from nitric acid or excess of HCl . 35 grams of gold require about 200 c.c. of fresh *Aqua Regia* which can be prepared by mixing 3 parts of strong HCl with one part of strong HNO_3 before use.

For making 100 grams of liquid gold with 12 per cent gold content, the following ingredients may be used.

1. Gold glance with 45 per cent gold	26.7 grams.
2. Bismuth resinate with 6 per cent Bi_2O_3 6.5 „
3. Chrome resinate with 4 per cent Cr_2O_3 1.2 „
4. Rhodium resinate with 3.5 per cent Rh.	... 1.2 „
5. Rosemary oil.	... 23.0 „
6. Fennel oil.	... 9.8 „
7. Asphalt dissolved in 50 per cent Nitrobenzene.	... 14.0 „
8. Colophony dissolved in 50 per cent Turpentine.	... 17.6 „
Total	... 100.0

Preparation of Gold glance:—Take the sulphur balsam in a large porcelain basin and add to it with constant stirring sufficient gold chloride solution to give

45 per cent gold content. The gold solution should be sufficiently diluted. Warming of the mass may be necessary for vigorous stirring. Leave it for 24 hours to complete the reactions.



Decant off the liquid collected on the top of the black mass and wash it with hot water five or six times till the wash water is free from HCl. Collect the wash water as it contains some gold solution. Remove all moisture from the dark mass by rubbing with a pestle and warming occassionally when it is ready for mixing with the other ingredients.

Mix all the ingredients of liquid gold with the gold glance prepared as above and shake well preferably in a mechanical shaker, for several hours. Then keep the solution in a well corked bottle. The resinate solutions should be prepared as per process mentioned before. The asphalt solution helps in painting the liquid with brush.

Various coloured lustres can be produced by mixing liquid gold with other metallic resinates.

1. *Blue lustre.*

Liquid gold ... 1 part.

Tin resinate ... 4 parts.

Bismuth resinate 10 parts.

2. *Green lustre.*

—

Blue lustre ... 3 parts.

Uranium Resinate 2 parts.

3. *Pink lustre.*

Liquid gold ... 1 part.

Tin resinate ... 1 part.

Bismuth Resinate ... 4 parts.

Varying the proportions of different ingredients, a variety of shades can be produced at the will of an intelligent painter.

Decorations. Besides the applications of coloured glazes or metallic lustres on glazed wares, various other means are used for decorating pottery wares. The principal methods may be classified under the following heads.

1. Painting. 2. Spraying. 3. Printing.
4. Chromolithography. 5. Dusting. 6. Engobing.

The painters brush is the easiest instrument for applying suitable colours to pottery wares. In order to use the brush freely, the colours must be mixed with some liquid medium possessing such binding power, that the colours will stick firmly on the surface of the wares even after the liquid has dried up. The common liquid used for this purpose specially for painting on biscuit wares, is known as *fat oil*. It can be prepared by boiling together on a steam bath.

Oil of turpentine...	7 parts.
Rosin	2 parts.

Or by mixing thoroughly, about one per cent of thickly boiled linseed oil with turpentine.

Colours well mixed with this medium, can be applied to the wares with the greatest ease without being absorbed into the wares. The oil of turpentine quickly evaporates, leaving the resin or linseed oil to keep the colours fixed to the wares without the fear of the

decorations being spoilt by the carbonisation of the organic matters.

For painting on glazed articles, a little glycerine or gum water can be used.

Spraying. Colours can also be sprayed on biscuit or glazed wares by a needle sprayer using compressed air at a pressure of 20 to 30 lbs. per sq. inch.

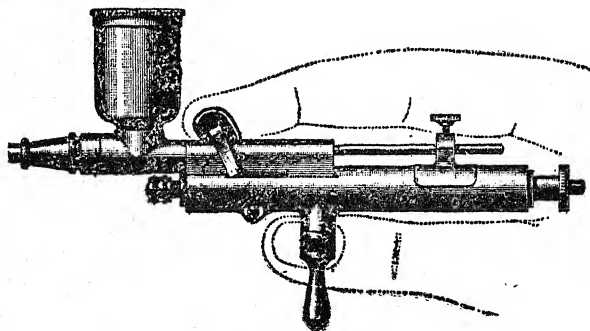


Fig. 18. Needle sprayer for colours.

For biscuit wares the colour should be well mixed with turpentine oil and a little of fat oil to a thin liquid state.

For glazed wares, the enamel colour is mixed with water to such a thick consistency that a stick can stand erect in it.

Printing. Earthenwares are often decorated by printing at the biscuit state with coloured designs. For this purpose blue and green colours are generally used, as these colours can stand well, the high temperature of

subsequent glost firing. The following recipes can be used for making good printing colours.

Printing Blue.

Cobalt oxide...	60
Flint ...	20
Felspar ...	10
China clay ...	10

Printing Green.

Chrome oxide ...	32
Cobalt oxide ...	8
Alumina...	25
Felspar ...	15
Flint ...	18
White lead ...	2

Calcine the above mixtures at about 1100°C, grind very fine so that the ground material easily pass through a 200 lawn. Wash the colour thoroughly before use.

In order to facilitate printing, the colours should be well mixed with a printing oil as thick as possible. The *printing oil* is prepared in the following way,

Best linseed oil	1/2 pint.
Gum mastic	1/2 oz.
Gum Amber	1/2 oz.
White lead	1/2 oz.

Slowly boil the above ingredients to the consistency of treacle. Store it in a place out of contact with air. The longer it is stored the better.

A good old method of making printing oil is given below.

Boil a mixture of a quart of linseed oil with about half pint of rape oil and while still boiling add an ounce of rosin and an ounce of white lead and Stockholm

tar. The boiling should be conducted over a clear fire without flame and it should be continued until the mixture becomes 'ropy' so that by dropping it on a cold plate and trying the tenacity with the finger it should 'rope' 5 or 6 inches or more when the finger is lifted.

Let the oil then cool and when the bubbling has just ceased stir in half a pint of spirit of tar. The older the linseed oil the better and less boiling is required with it. The oil so prepared improves with keeping. A good printers oil should give a solid print which sticks to the ware and does not wash off. The oil should not skin over if allowed to stand a few hours.

The function of the rape oil is to make the linseed oil less harsh. Gum mastic, Oregon balsam, Canada balsam or rosin oil is sometimes added to stiffen the mixture but if too much of these agents be added the colour is liable to come off in washing.

Stockholm tar (wood tar) or asphaltum makes the colour stick better to the wares and makes them washable. White lead, lead acetate, manganese borate or oxide in very small amounts make the oil sticky but care must be used or the oil will skin over too quickly.

The colour well mixed with the prepared oil, is first, thinned by warming on a hot plate, and then spread with a flat knife or spatula on the engraved plate, generally made of copper. The colour enters into the engravings and the extra colour is scraped out with the same knife. The surface of the plate is then cleaned with a thick pad leaving only the colour that has

entered inside the engravings. Now, a piece of fine tissue paper is thinly brushed with a soft soap solution known as the *size*, and the paper placed carefully on the engraved plate with the soap side touching the plate. The whole plate is then pressed under a roller thickly padded with felt. Then the plate is warmed again and the tissue paper taken out of it, the paper acquires the impression of the engravings.

The *printed paper* thus obtained is placed on the biscuit ware, smoothed with a piece of felt and then rubbed with a hard brush and kept away for sometime to allow the porous ware to absorb the colour. The articles are then dipped in a tub of water till the tissue papers begin to separate from the ware when the papers are wiped out gently with a piece of sponge.

After drying, the wares are ready for the glaze dip.

Printers size can be prepared by boiling one pound of soft soap with an ounce of soda ash in a gallon of water.

In large factories the printing is done in roller machines. Only two or three colour designs can be printed together in this process.

Printing can be made both on biscuit wares and glazed articles.

The biscuit printed wares are first sponged with a very dilute glaze slip acidulated with sulphuric acid before they are dipped into the proper glaze slip. This preliminary treatment breaks up the oil film of

the prints and renders the unprinted surfaces of the wares less absorbant, so that the glaze does not skip off

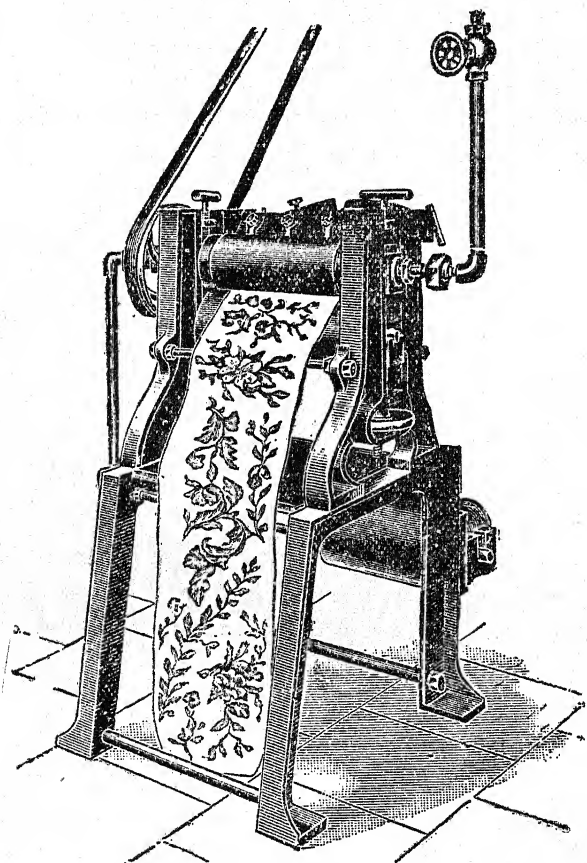


Fig. 19. Pottery printing machine.

from the oily surfaces of the prints and the whole surface of the ware is uniformly glazed.

For printing on glazed wares, the colours must be properly fluxed, before mixing with the printing oil.

In the previous process of printing from copper or steel plates only two or three colour-designs can be reproduced and those also merely in outlines or with shades only. But by the process of chromo-lithography it is possible to reproduce designs of any number of colours, by the simple transfer method and the designs appear as if they were hand painted. This process is used mainly for glazed ware.

Chromo-lithography. In this system of decoration, special printed papers with multi-coloured designs are used to transfer the designs on the glazed wares. In making these papers the designs are etched on stones, one stone for each colour. The colours are mixed with special varnish for printing. Before printing the paper is coated with a very thin layer of soluble substances separating the colour prints from the paper, so that the paper can be removed easily after the transfer has been applied to the ware. The materials used for this intermediate layer are generally easily soluble gums, glue and dextrine, or starch paste and gum tragacanth, which swell up quickly when moistened with water.

The transfer litho papers are made by special firms and it is advisable to buy these papers from a reliable maker. The design is transferred from the paper to the glazed ware in the following manner.

Cut out the design from the paper leaving the unprinted portions and dip it in water for a moment or so. The water will penetrate through the paper and

cause the gummy layer to swell while the printed portion is unaffected by water due to the presence of a protective varnish.

Now the parts of the glazed ware to be decorated are painted with a lacquer varnish and allowed to dry until the surface is very tacky. The transfer paper is then applied on the tacky surface with the picture side down wards, and pressed evenly from the centre outwards to remove all air bubbles. Place the ware in a tub of water and after a little while the paper will detach itself due to the intermediate layer being dissolved out. Take the ware out of the tub and dry. It is then ready for the enamel fire. If there is any imperfection in the decoration due to careless transferring, the defects can be removed by touching with painters brush.

The lacquer varnish generally known as *lithographic size*, can be prepared by boiling together the following ingredients till the liquid becomes thick and tacky.

Terpentine oil	2 gallons.
Rape oil	$\frac{1}{4}$ gallon.
Clear Rosin	5 lbs.
Canada balsam	$\frac{1}{2}$ oz.

Some Continental litho-papers are gummed on the surface and do not require the use of size on the ware.

Dusting. For this method, the glazed ware is first coated uniformly with a specially prepared oil by means of a brush and allowed to dry a little. Then the colour in the form of fine powder is dabbed with cotton wool on this sticky coating and the extra colour which does not

adhere to the ware is brushed off. The success chiefly depends on uniformly laying the oil and the colour.

The special oil used for this purpose is known as *ground laying oil*. Boil slowly over a mild fire till the liquid becomes thick :—

Linseed oil	1 part.
Gum mastic	1 „
Red lead	$\frac{1}{2}$ „
Rosin	$\frac{1}{2}$ „

Dilute the liquid with turpentine oil when required.

Engobes. These are specially prepared bodies either white or coloured in any desired way for coating on clay wares. The main purport of engobing is to cover the surface of a coloured body with a white coating as used for sanitary wares made from fire clays but in special cases coloured engobes are used for decorating earthenwares and making polychrome tiles.

The essential condition of engobing is that both the body of the ware and the engobe should behave similarly at all temperatures, otherwise the engobe after firing would either crack or chip off from the main body. If the engobe has the proper composition it will attach itself firmly to the ware, and retain its cohesion even under the strongest fluctuations of temperature. If the engobe however cracks or springs off under similar conditions it is evident that the coefficient of expansion of the engobe does not tally with that of the body of the ware. In such case the composition of the engobe should be adjusted in the same way as is done with defective glazes.

The main ingredients of white engobe are china clay, felspar and quartz. A small amount of whiting is sometimes used to increase the whiteness of the engobe. A few trials, adjusting the amount of silica will bring the desired concordance between the engobe and the body.

Coloured engobes are best made from the same composition as used for the body of the wares. If the body composition is too dark in colour, a little white burning clay may be mixed with it to lighten the shade. Metallic oxides or stains are used for producing different shades of colour as mentioned for producing coloured glazes.

The engobe mixture is mixed with water to form a slip. Lightly cast wares are first baked and then dipped into the engobe slip. Air dried wares lack the necessary absorbent power and strength for direct dipping in the slip. The application of engobes requires a good amount of skill so that all parts of the ware may be covered evenly. For heavy sanitary ware the application of engobe is best done by spraying. For the application of different coloured engobes, the slip is kept in a small rubber bag provided with a nozzle. The bag is pressed between the fingers and the palm of the hand, and the slip comes out through the nozzle for application as desired.

As soon as the engobe is dry it is fired in the biscuit oven. The engobed articles are then glazed and fired again.

CHAPTER V.

PORCELAINS.

The potters art was known to prehistoric man and is probably the oldest of arts practiced by mankind. Porcelain is the highest attainment of man in the field of ceramic arts. It was developed by Chinese potters after more than a thousand years of painstaking experiments working under the protection and patronages of their emperors.

To the eye, porcelain is a beautiful non porous, white or bluish white body of very fine texture, translucent in thin section. The impermeability of porcelain distinguishes it from common pottery and the translucency makes it differ from stoneware. When clipped, porcelain shows a conchoidal fracture like glass, in contrast to the rough and irregular fracture of the common or semivitreous pottery. When struck, a good porcelain cup gives out a high pitched musical note. This sonorous note is largely due to the use of potash felspar in common porcelain composition. If the potash is replaced by soda, the musical note will be short and flat. Common porcelains have porosity always less than one per cent.

The cause of translucency of porcelains was attributed by Mellor to the penetration of the molten flux into the porous particles of China clay in the same manner as a piece of blotting paper becomes translucent

when soaked with oil. The particles of ball clay generally close their pores before the felspathic flux begins to melt; consequently, if a porcelain body contains more than 5 per cent of ball clay in the mixture, its power of translucency is greatly impaired.

The glassy matrix of porcelains have nearly equal index of refraction as that possessed by mullite crystals. The average value for mullite being 1.648, and of light flint glass 1.65, and of quartz 1.543. It is evident therefore, that to increase the translucency, there should not be any free quartz particle left in the glassy matrix, the presence of which will diffuse light and produce milkiness or opacity. The translucency of porcelains greatly increases after the body has been glazed.

Porcelains are divided into three main classes :—
(a) Hard or felspathic porcelain. (b) Soft or glassy porcelains; and, (c) Bone china or English porcelains.

Hard porcelain was first made in China and afterwards brought to Europe. It contains about 2 to 5 percent of potassium oxide used as felspar. It is usually covered with a glaze which vitrifies at the same time with the body at temperatures ranging between 1300°C and 1600°C.

Soft porcelains are very different from the hard ones, and are mainly composed of glassy frit. They are burned at much lower temperature and coated with a softer glaze. This kind of porcelain was first made in Italy in the attempt of imitating the Chinese porcelain. It is more in common with glass than with real porcelain or pottery.

Bone China or phosphatic porcelain is only extensively manufactured in England where it was discovered during trials for making a body similar to Chinese hard porcelain. It requires much lower temperature for burning, than that for hard felspathic porcelain and it is easier to decorate it. The body and glaze of bone China are not matured together, but on the other hand the body is fired at a higher temperature than the glaze. The special characteristic of this porcelain is the large amount of calcined bone or *bone ash* used in the body.

Pyro-Chemical reactions.

Hard porcelain bodies are made mainly from felspar, quartz and kaolin. In England Cornish stone and flint are often substituted for felspar and quartz. For bodies fired at a relatively high temperature, felspar is quite superior to Cornish stones. The felspar body is more translucent, more vitreous and less liable to blister. On the other hand, a body fired at a lower temperature, can be made from Cornish stones and is particularly strong and suitable for making large vessels. It is important to note that felspar is less suitable for making the low temperature domestic wares as the felspar body tends to assume a glassy structure and breaks easily when struck.

On heating, orthoclase gradually softens and finally forms a very viscous liquid which binds the other materials and gradually dissolves them. It has been estimated that between 1400°C-1460°C felspar—melt can dissolve about 70 per cent of its weight of quartz or 10

per cent of clay and still form a clear glass. When more clay is present it forms well defined mullite needles.

Flint has a decided advantage over quartz ; in porcelain body that on one calcination it turns to a white, low density (Sp. Gr. 2.24) form which is easily crushed to fine powder, while quartz on repeated calcination undergo only relatively little change and is still hard to grind. On heating quartz powder to 870°C it is converted into β tridymite with a specific gravity of 2.27. On further heating to 1470°C, it is converted into β cristobalite with sp. gr. 2.34. When heated to 1685°C the cristobalite melts into a quartz glass with a sp. gr. of 2.21. All these silica transformations are reversible and when a burned porcelain is cooled slowly the silica which has not gone into solution in the felspathic melt, forms crystals of quartz again. The low density form of silica dissolves in felspathic glass more quickly than the high density ones. Hence calcined flint will dissolve more quickly and completely than calcined quartz. The presence of free quartz grains in the final porcelain, may cause cracking on reheating the ware due to the expansion of the quartz for its inversion to forms of greater volume.

This is specially objectionable in the case of porcelains subject to frequent heating such as spark plugs, laboratory and cooking porcelain and thermo-couple protection tubes.

A material of great promise in this respect is fused quartz which dissolves more readily in the porcelain glass allowing a lower firing temperature than of flint even.

When we consider the clay-felspar-quartz mixtures heated to suitable temperatures we find that the compositions of commercial feldspathic porcelains lie within the parallelogram ABCD shown in the figure.

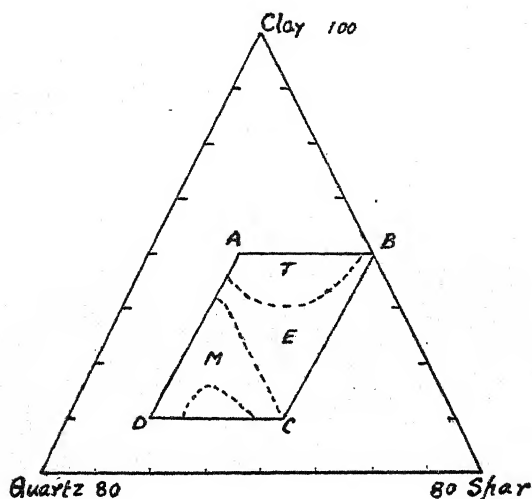


Fig. 20 Composition of commercial porcelain.

The main problem in porcelain burning is to develop as much well defined mullite crystals as possible embedded in a glassy matrix. According to Klein the quartz grains are only slightly attacked at 1340°C while kaolin dissociates into mullite at this temperature. At 1460°C the attack on quartz by the feldspathic melt becomes very much pronounced and kaolin goes into solution upto 10 per cent. More clay forms well developed mullite needles. Between 1380°C to 1400°C a large portion of the quartz is dissolved and most

of the clay is changed to mullite. It would seem then for average porcelain mixtures the best ware is produced at 1460°C although for common porcelain, firing at 1400°C is sufficient. High clay and low felspar bodies would require higher temperature while high felspar and low clay bodies would mature at lower temperature.

A good piece of properly fired hard porcelain should consist of a highly siliceous potash—alumina glass, containing about 30 or more per cent well developed mullite needles and amorphous mullite. A few remnants of quartz grains might be present but a large amount of it is objectionable specially for those porcelains which should stand repeated heating during use. Spark plugs contain more than 40 per cent of mullite and no free quartz. Typical chemical porcelains contain about 40 per cent and high tension electrical porcelains contain about 35 per cent of mullite.

A few typical compositions of felspathic porcelains are given below.

	1	2	3	4	5	6
Silica. ...	70.5	78.8	66.6	59.4	58	68.27
Alumina. ...	20.7	17.8	28.0	32.6	34.5	26.63
Iron oxide. ...	0.8	0.6	0.7	0.8	—	0.89
Lime. ...	0.5	0.2	0.3	0.3	4.5	0.69
Magnesia. ...	0.1	—	0.6	—	—	0.86
Potash oxide.	6.0	2.2	3.4	5.5	3.0	2.31
	98.6	99.6	99.6	98.6	100.0	99.65

1. Chinese porcelain.
2. Japanese porcelain.
3. Berlin hard porcelain.
4. Meissen hard porcelain.
5. Sevres hard porcelain.
6. Royal Berlin chemical porcelain.

The second type of porcelain generally known as soft paste porcelain is an intermediate product between glass and true pottery. It is composed of a glassy matrix interspersed with large amount of insoluble materials which diffuse the light and produce the whiteness or milkiness in the body. In the race to discover the secret of Chinese porcelain, a material so greatly superior to their own relatively coarse and heavy earthenwares, the European potters used various sorts of materials in their compositions. The various types of soft porcelains as evolved in different countries in different periods can be classified under the following groups.

1. *Glassy porcelain.* This was made in the 16th century using highly calcarious glassy frit mixed with a small amount of clay. The body was very non plastic and difficult to mould. When the dangerous fluxing effect of lime in firing the body was discovered the percentage of lime was greatly reduced and replaced by alumina or China clay and the improved soft porcelain of Sevres was produced. This improved porcelain require harder firing than the previous ones but the body is much superior in every respect,

The following are a few typical analyses of soft paste porcelains of the glassy type.

	1	2	3	4
Silica ...	72.5	72	76.16	78.36
Alumina & Iron	2.7	5	4.3	2.45
Lime ...	13.6	15	9.28	12.73
Magnesia ...	0.3	—	—	—
Alkalies ...	10.9	8	3.76	6.46
Lead oxide ...	—	—	6.5	—
	100.0	100.0	100.00	100.00

1. Typical sheet glass composition. 2. Early French porcelain. 3. Longton porcelain of 1760. 4. Sevres soft porcelain.

2. *Soapstone porcelain.* In some parts of England specially at Bristol, Swansea, Coughley and Worcester, China clay was replaced partly or wholly by soap stone. A few typical analyses of all-soap stone porcelain containing various amounts of soapstone are given below. Soap stone is not used nowadays in ordinary wares, and its use is restricted to some special types of porcelain for specific purposes.

	1	2	3
Silica ...	67.62	74.22	81.56
Alumina ...	4.61	8.5	8.9
Phosphoric acid	2.0	0.2	0.33
Lime ...	2.64	2.78	0.7
Magnesia ...	13.28	7.62	4.26
Alkalies ...	2.76	3.55	3.88
Lead oxide ...	8.01	3.73	—
	100.92	100.6	99.63

1. Bristol porcelain of 1750, containing about 40 per cent soapstone. The presence of

lead oxide indicates that the fusible fluxes were introduced in the form of broken flint glass.

2. Caughley porcelain of 1780 containing about 22 per cent soapstone.
3. Swansea china of 1817. It contains about 13 per cent of soapstone.

The use of soapstone in all these old porcelains was to introduce a white plastic material in place of china clay which was rather rare at that time.

3. *Bone China*. This is the only type of soft porcelain of modern industrial importance. This phosphatic porcelain was exclusively manufactured in England and the word *china* is used for all translucent soft porcelain. The chief advantages which bone china offers to the potters are—the greater plasticity of the body mixture, the lower firing temperature and the greater range of colours available for decorating it. Average bone china of to-day generally contain 28-30 per cent of properly calcined bone ash but in older days much more was used. A few old compositions are given below.

	...	1	2	3
Silica	...	43.58	41.94	47.80
Alumina	...	8.36	15.97	26.49
Lime	...	24.47	24.28	13.25
Magnesia	...	0.60	0.2	—
Phosphoric acid		18.95	14.96	9.85
Alkalies	...	2.05	1.96	3.27
Lead oxide	...	1.75	0.36	—
		99.76	99.67	100.66

1. Bone china from Bow of about 1760. About 48 per cent bone ash.

2. Bone china from Derby of about 1790, containing about 38 per cent bone ash.

3. Swansea china of about 1820. About 25 per cent bone ash.

4. *Biscuit porcelain or Parian ware.* This is a special type of soft porcelain without a glaze, for making statuette and figures. The composition is generally made of clay and felspar which on firing produce a body of dull brilliance resembling the beautiful marble of Paros, whence the name of *Parian ware*. The body may be sometimes coloured to imitate natural minerals like malachite, lazurite etc. The absence of quartz in these bodies is specially advocated by Seger to avoid the disagreeable fatty gloss prominent on the projecting parts.

Preparation of bodies. The raw materials except the kaolin are ground very fine in big cylinders filled with flint pebbles. The grinding takes about 40 hours. The ground materials are then run down through a rough sieve into *blungers* or tanks provided with powerful agitators. These blungers are generally situated under the floor level. The kaolin is added here into other ground materials and thoroughly mixed for several hours. The clay slip is then allowed to run into another tank passing through an electro-magnet, from where it is pumped into the filter presses for dewatering.

The cakes when taken from the filter press have generally the consistency of soft paste. In some works they are allowed to sour in a dark room before they

are sent to the kneading machine, to increase the plasticity of the body. A kneading machine is shown in fig. 10. This operation of kneading takes about 45 minutes and the mass is much more plastic and workable after this operation.

It would be impossible to describe the making of all articles of porcelain within the scope of this book, but it may be interesting to follow one process such as the making of common double cup electrical insulators.

The body from the kneading machine is first passed through another machine called extruding machine from which it comes as a solid round mass like sausage, and cut into pieces with a wire according to the size required. If this extruding machine is not properly designed and controlled, lamination trouble may develop here which will show only after firing.

Each cut piece is then placed inside the mould, a piece of cloth placed on it and the clay is pressed into the mould by a hand press having a wooden plunger. It is then jolleyed, and the less water used at this stage, the better it is for drying. Too much water used in making, is the chief cause for the drying cracks of this kind of wares.

The articles are then allowed to dry in the moulds and after about an hour they are taken out from the moulds and placed on wooden planks to dry till they are leather hard.

The inner ring is joined at this stage with clay slip by one man while another turns the neck and sponges the body, so that a pair of workers helped by a boy or

a woman make about 3,000 insulators, about 6 inches high per week in Germany. In England and in India the inner ring is jolleyed together with the outer body in the same operation.

The screw is cut on the leather hard articles while they rotate on the jigger. The borer is dipped in oil and slowly pressed in the hole. The jigger is then stopped and made to rotate in the opposite direction, while the borer is slowly taken out. On big articles, screws are cut by hand machines.

Multiple-cup insulators, are made in several parts which are then joined with clay slip while still in green condition.

Semi plastic body is made, specially for small electrical articles by first drying the cakes from the filter press in special hot rooms and then powdering them in a disintegrating mill. Dry broken articles are also used up with this body. The powder is mixed with water and oil in a mixer and made into such consistency that when a handful of them is pressed, the powder forms a lump but does not wet the hand.

About 300 lbs. of dry powder is mixed with $4\frac{1}{2}$ litres of oil. The oil is made up from :—Thin oil, or crude petrol, 4 parts. Thick oil, or residue of olive, linseed or castor oil, $\frac{1}{2}$ to 1 part.

Water is added according to the nature of the dry powder. The prepared mass is again passed through a centrifugal disintegrater where any lump formed during mixing is broken and lawned together and the mass is ready for use.

The mass is then pressed into shapes in a pillar press fitted with dies of required shapes.

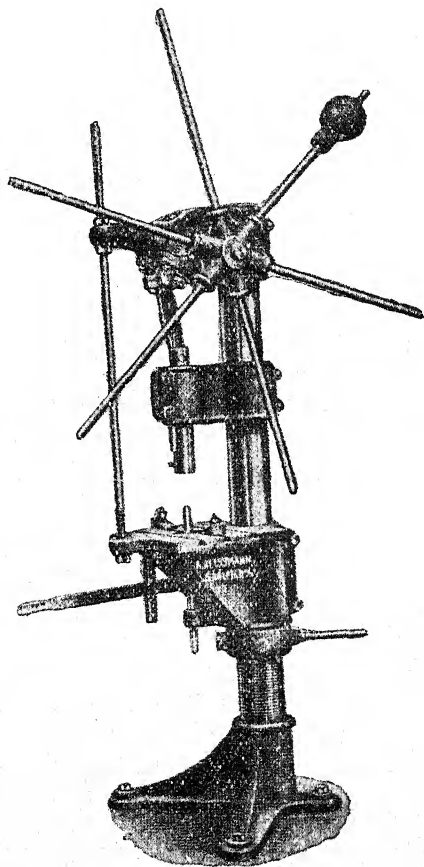


Fig. 21 A pillar press for porcelain.

Casting slip is prepared from the pressed cakes in a separate blunger. The right amount of water together with the required quantity of electrolytes are added in

the blunger and thoroughly mixed till the liquid slip is homogeneous and weighs about 35 ozs. per pint. This slip is then allowed to run into a separate tank provided with an agitator to prevent the ingredients to separate, before it is pumped to the casting benches.

In casting round articles, the moulds are placed on a rotating table or disc, which is slowly turned when the slip is poured into the mould. If too dry moulds are used, the first or second pieces cast from them, generally crack in the mould but when the moulds get moistened, the pieces come out quite well. When moulds get too damp the cast pieces do not come out of them easily and the moulds are to be sent for drying. When the mould has some intricate parts and the casting show some trouble a little dusting of lycopodium powder from a muslin bag often helps in delivering the articles from the mould.

Hollow brass tubes are generally used for punching holes in the cast wares. Cast pieces when out of the moulds are placed on plaster bats and allowed to dry on wooden rocks erected near the casting benches. The wares are cleaned and polished by the same girls who made them.

Drying of open bodies like porcelain, does not present any special difficulty. They are usually dried in the casting shops which are artificially kept warm during winter. The temperature within these workshops during winter is between 20° to 25°C and that in summer between 25° to 30°C in central Germany. Hollow wares generally take 4 to 7 days, and big solid

articles such as high tension insulators take from 10 to 15 days for drying according to the season of the year. The final stage of drying is judged by the feel of coldness; a *bone dry* article, which has whitened to a great extent does not feel cold to the touch at all.

Body Compositions. General porcelain bodies can be divided into four different groups:

(1) Bodies with a very high clay content, but low in quartz and felspar, in which the fluxes are supplemented by a considerable addition of calcium carbonate.

Sevres body.

Clay substances	...	66.37
Quartz	...	12.05
Felspar	...	15.11
Calcium carbonate	...	6.47

(2) Bodies high in felspar, whose fluxing action is intensified by a small addition of calcium carbonate.

Limoges body. Karlsbad body.

Clay substance	...	41.0	51.97
Quartz	...	19.5	24.50
Felspar	...	38.0	21.93
Calcium carbonate	...	1.5	1.60

(3) Bodies with low content in clay substance but moderately high in felspar.

Japanese body. Copenhagen body.

Clay substance	...	31	47
Quartz	...	41	20
Felspar	...	28	33

(4) Bodies with a high clay content and moderate proportions of quartz and felspar.

	<i>Berlin body.</i>	<i>Belgian body.</i>
Clay substance ...	53	57.9
Quartz ...	20	26.0
Felspar ...	27	16.1

A few practical formulas of table ware porcelains are given below.

	1	2	3	4	5
China clay ...	48.0	48.3	43.5	40.5	40.5
Felspar ...	37.5	48.5	40.0	36.5	23.5
Quartz ...	13.5	1.7	13.0	23.0	35.5
Magnesite. ...	0.5	—	—	—	0.3
Zinc oxide ...	0.5	—	—	—	0.2
Pitcher (Bisc)	—	1.5	3.5	—	—
	100.0	100.0	100.0	100.0	100.0

The above bodies mature between cones 13 and 14.

The felspar used in the above bodies has the following composition. Body no. 5 is used for making doll head etc :—

SiO_2 — 73.43. Al_2O_3 —15.39. Fe_2O_3 —0.02.

Alkalies—10.6. CaO — 0.14. loss— 0.2.

A suitable glaze for the above bodies is computed from the following :—

Calcined quartz.	...	37
Lime spar.	...	12
Felspar.	...	6
Kaolin.	...	6
Glost pitcher.	...	39
		<hr/> 100

Electrical porcelain. Hard vitrified porcelains when glazed with a proper glaze make very efficient insulators for high tension electric current. The only competitors for hard porcelain in this line are steatite and stoneware. Steatite has got the advantages over hard porcelain that its contraction is very low and its mechanical properties are better than those of hard porcelain.

An unfortunate disadvantage of porcelain and stone ware insulators is their great difference in quality when obtained from different firms, and it is by adhering to one firm only, that one can get articles of constant quality.

Physical constants of different porcelains.

1. *Specific Gravity.*

Royal Berlin porcelain	...	2.29.
Meissen porcelain	2.49.
Sevres porcelain	2.24.

2. *Coefficient of linear expansion.*

0.000003 to 0.000004.

3. *Thermal conductivity.*

0.002

4. *Electrical conductivity.*

At 160°C— 0.58×10^{-12}

At 600°C— 0.62×10^{-6}

At 1000°C— 1.00×10^{-6}

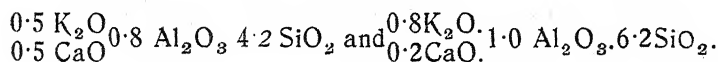
5. *Dielectric constants.*

Hard porcelain	...	5.73
Stoneware	...	5.17
Steatite	...	5.40

E. Gerold found that the glaze has an important influence on the mechanical properties of hard porcelain. A glaze usually increases the elasticity of the porcelain while the tensile and impact strengths also improve by the application of glaze. The glaze on a high tension electrical porcelain should be harder than quartz, that is above 7 on Moh's scale of hardness. Such a glaze will have very high resistance to weather.

The porosity of the body of a high class insulator should be so low that the fractured surface should not be stained if red ink is poured on it, allowed to remain for several hours, and then washed off. Cheap insulators will not stand this test. According to Watkin, a porcelain having a porosity of 0.016 per cent by weight does not decrease in resistance at all after 14 days immersion in water; but one having 0.05 per cent porosity, falls rapidly in resistance by such soaking.

A. S. Watts considers the best electrical porcelain body to have a composition between.



The following are some practical compositions of insulator bodies and glazes.

Composition of Bodies.

	1	2	3	4
Kaolin. ...	45.	48	53	53.
Felspar ...	30	35	16	10
Quartz ...	25	17	21	20
Steatite ...	—	—	10	17

Body no. 1 is suitable for telegraphic insulators and matures between cones 12 and 13. Nos. 2, 3 and 4 are high tension electrical porcelains maturing between cones 13 and 14.

Glaze compositions.

			1	2	3
Felspar.	42	40	34
Quartz	41	42	45.5
Dolomite.	10	9	7.5
Kaolin.	7	9	13

Glaze No. 1 is suitable for the telegraphic insulators while the others are for the high tension bodies. About 20 to 30 per cent of glost pitcher is generally used with these glazes for economy. High tension insulators are generally coloured deep green or brown to distinguish them from low tension ones.

Steatite Porcelain. As mentioned before, these porcelains have better properties for electrical insulators than true felspathic porcelains. According to L.E. Thiess (1937) a true steatite body is composed of a mixture containing more than 70 per cent of talc or soap stone, a natural hydrated magnesium silicate. The remainder of the mixture consisting of such substances which bring about complete vitrification by eutectic melts, and crystallisation. The finished product consists of a densely felted structure of magnesium metasilicate.

Steatite bodies containing about 50 per cent clay have very short firing range. In such bodies the

vitrification and fusion temperatures are very close together but when the steatite content is more than 70 per cent the firing range is about 2 cones, which is sufficient for a properly controlled furnace.

Talc used for making true steatite bodies must be carefully selected. Those with flaky or foliated structure do not develop plasticity when ground wet and form lamination cracks when pressed in dies. Talc containing high CaO are not suitable.

Since high talc bodies are very lean, wet grinding in ball mills develop better plasticity than blunging. A small amount of bentonite or gums considerably increases the working property and dry strength of these talc bodies. The softness and the non abrasive character of these bodies cause very little wearing of dies and moulds and make them very suitable for automatic pressing.

The analysis of a typical true talc body is given below.

SiO ₂	—63·5
MgO	—28·5
Al ₂ O ₃	—6·0
Alkalies	—2·0
	<hr/>
	100·0

True talc porcelains can be prepared from the following compositions.

Good Steatite	—	82	85	86
Plastic Kaolin	—	12	13	10
Potash felspar	—	6	2	4
		100	100.0	100.0

These bodies mature between 1350—1400°C.

The total shrinkage at 1300°C is less than 12 per cent and the porosity of the body at 1300°C is less than one, and at 1400°C nearly nil.

Effects of composition on electrical porcelains. are summarised in fig. 20 given on previous page. T represents the maximum resistance area for thermal changes. E shows the maximum dielectric power area, and M the best mechanical resistance area. The felspar content in electrical porcelain bodies should be between 25 to 35 per cent while the clay should always be above 40 per cent.

Thermal changes. A good insulator should be able to resist rapid changes of temperature caused by the heat produced by high tension current, changes of weather, rains and frost. For the same coefficient of expansion, coarse grained bodies are less sensitive to sudden temperature changes than bodies with glassy fracture. High proportion of quartz in the body reduces the resistance to thermal changes. The quartz can be replaced by china clay, sillimanite or zirconia with advantage.

Electrical conductivity. The conductivity of porcelain at the ordinary temperature is very low but at high temperature the conductivity increases rather rapidly.

Based on this property of porcelain, a special test is applied known as *Te value*, which is the temperature at which the electrical resistivity is reduced to one megohm per cubic centimeter. Good insulators may deteriorate with use and what appears a non-porous body acquires a certain porosity after some time. The alternating electrostatic field sets up a kind of vibratory motion in the crystals which may rupture along the lines of contact of the crystals with the surrounding matrix.

E. Watkin has found out that increase in the amount of china clay in place of flint increases the specific resistance, but substitution of ball clay for china clay has a deleterious effect on the electrical properties of porcelain. Substituting steatite for felspar increases greatly the specific resistance of the body.

According to R. Twell and C. C. Lin quartz may be reduced by sillimanite, alumina, and zirconia to increase the resistivity of the porcelain. Substitution of steatite for felspar greatly increases the electrical resistance but has little effect on the dielectric strength.

Much depends on the form of the insulator. It should be so shaped that the length of the leakage path along the surface should be as great as possible. Single-cup insulators are seldom if ever used for power transmission. Multiple-cup forms are preferred, as a flaw in one cup does not destroy the whole insulator.

Dielectric strength. An efficient insulator should have a high resistance to puncture by strong electric sparks. According to E. Rosenthal, a piece of hard

porcelain 2.5 m.m. thick and fired at cone 16, will resist a current up to 40,000 volts. The influence of body mixture on the dielectric strength of porcelain according to the same author is, when kaolin content is kept constant at 55 per cent, increment of felspar at the cost of quartz increases the dielectric strength till the ratio of felspar to quartz is 25 to 20, but further increment of the former diminishes the dielectric power of the body.

The body should be properly vitrified to get the maximum dielectric strength. For low temperature bodies high felspar content at the cost of quartz gives better result but for high temperature bodies reverse is the case. Potash felspar is superior to soda felspar in this respect. Lime does not give good result but beryllium oxide with potash or soda base gives better result. B.S. Radclif has found that a porcelain body containing 6-8 per cent of lime, burned at the same temperature and having the same porosity as a potash porcelain has only half the dielectric strength. Hence the proportion of lime should be kept as low as possible.

Mechanical strength. The material should be as capable of resisting tensile, compressive and impact stresses as possible. According to Rosenthal, when felspar is increased at the cost of quartz, the compressive strength of the body increases till their proportion is equal, but further increase of felspar diminishes the strength. The clay content is kept at 55 per cent for, when it is increased to 65 per cent, both the mechanical and dielectric strengths of the body are consider-

ably reduced. Substitution of ball clay for china clay also reduces the mechanical strength. According to Bleininger the strength is increased by substituting zirconia for flint. When felspar is partly replaced by steatite, the proportion of glassy matrix in the porcelain is reduced with the increase in mechanical strength.

Chemical Porcelain. The hard paste Berlin porcelain body used for manufacturing evaporating dishes, crucibles etc. has a faint yellow colour. The average chemical composition of the body is :—

	<i>Berlin body.</i>	<i>French body.</i>
SiO ₂	... 67.5	61.61.
Al ₂ O ₃	... 26.6	30.01.
Fe ₂ O ₃	... 0.8	1.56.
TiO ₂	... 0.4	—
CaO	... 0.4	3.56.
MgO	... 0.5	—
K ₂ O	... 3.3	3.26.
Na ₂ O	... 0.7	—

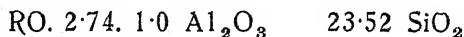
The absolute heat conductivity of chemical porcelain is greater than that of glass but the coefficient of expansion is less than that of ordinary glass, stoneware, or such other materials. Hence, this porcelain is able to withstand sudden changes of temperature. The melting point of Berlin porcelain corresponds to cones 30-31 (1680°C). The glaze on the body must resist alkaline solutions and should be so hard that when the ware is heated on the clay triangle with a blast burner,

neither the triangle nor the contents of the vessel should adhere to the glaze. The ware is thin, vitreous and translucent.

Introduction of sillimanite or talc at the cost of quartz reduces the free quartz crystals in the fired body which will minimise the chances of cracking on repeated heating and cooling of the ware. Alkalies have low heat conductivity and high thermal expansion values than lime and magnesia. Hence chemical porcelains should have as low alkali content as possible.

Soft Porcelains. The chief varieties of felspathic soft paste porcelain which are largely used for decorative wares and toys are Seger's porcelain and new Sevres porcelain.

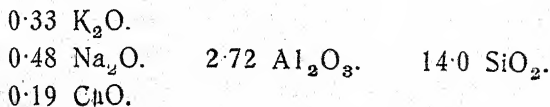
The former has the molecular formula for the body.



A similar body can be compounded from :—

Rajmahal kaolin	34.5
Mihijam Felspar	30.0
Calcined quartz	35.5

The French porcelain body has according to Vogt, the following molecular formula.



The bodies are biscuited at cone 9 so that they can be decorated under glaze. The glost firing is also low.

to allow the application of various coloured decorations, which is the essential feature of this type of porcelain.

The glaze used on the soft Sevres porcelain matures between cones 10 and 11, and has the following molecular composition.

0.85 CaO.

0.09 Na₂O. 0.5 Al₂O₃. 4.2 SiO₂.

0.06 K₂O.

A good imitation of Japanese glaze made by Dr. Seger, and used on Segers soft porcelain has got the composition.

0.3 K₂O. 0.5 Al₂O₃. 4 SiO₂.

0.7 CaO.

The maturing temperature of this glaze is between cones 9 and 10.

A soft felspathic porcelain maturing at 1300°C can be produced from the following :—

Body composition. Glaze composition.

Patherghatta clay...	45	Felspar ...	45
Ajmere felspar ...	35	Quartz ...	24
Quartz ...	17.5	Marble ...	18
Marble ...	2.5	Kaolin ...	13

A soft fritted porcelain is made from :—

Frit Mixture.

Body Mixture.

Borax ...	48	Frit ...	20
Quartz ...	24	Kaolin ...	40
Whiting ...	20	Quartz ...	25
Felspar ...	20	Felspar ...	13
Kaolin ...	8	Whiting ...	2

Biscuit the body at 800-900°C and apply the following glaze :—

Glaze mixture.

Felspar	37
Quartz	25
Barium carbonate	15
Whiting	10
Kaolin	8
Zinc oxide	5

This glaze matures at about 1200°C.

• A new material called Nepheline Syenite—a soda alumina silicate, is being used nowadays for pottery bodies and glazes. According to C. J. Koenitz (1939); by introducing nepheline syenite in reduced amount to replace potash felspar, a longer vitrification range is afforded which results in lower warpage. Bodies with nepheline syenite have higher pitch than regular wares. Fine grinding of nepheline syenite lowers the vitrification temperature and provides a longer maturing range; the warpage is decreased and the mechanical strength increased.

Crackled glaze. Crackling of glazes is due to a difference between the contractions of the glaze and the body during cooling. It is crazing of a special form, consisting of very fine lines with the appearance of fish scales with regular forms. These cracks are occasionally coloured with lamp black or other colouring agents for decoration.

The effect of crackling can only be attained by changing the compositions of the materials fired, either by altering the glaze or by altering the body. It is easier in practice to alter the glaze and keep the body constant. This is generally accomplished by increasing the alkalis and silica, and diminishing the alumina of the normal glaze. In the following two formulas are given the chemical compositions of a normal and a crackling glaze derived by the above rule.

Normal. Crackling.

Silica	...	66.10	79.53
Alumina	...	14.50	11.87
Alkalies	...	3.50	5.65
Lime	...	15.90	2.95

The crackling glaze was compounded from the following raw-materials.

Pegmatite	...	51 parts.
Sand	...	38 „
China clay	...	6 „
Chalk	...	5 „

The body most suitable for this particular glaze has the composition of—silica 66, alumina 27, and alkalis 7, maturing at cone 12.

The method of glazing is normal. The glaze ought to be of medium thickness. The thickness of the glaze affects the dimensions of crackling. This can be learnt only by experience. To increase the size of the scales, add some normal glaze to the crackling one and the greater the addition the larger the scales. The body

ought to be thicker than usual, so that it can stand the strain caused by the difference of contractions of the glaze and the body, and can avoid all chance of rupture. The Chinese were adept in this type of porcelain.

Bone China. The raw-materials used by English potters for making bone china are—china clay, ball clay, Cornish stone and bone ash. The following are some recipes for making bone china.

China clay	...	40	30	23	35
Ball clay	...	8	6	10	—
Cornish stone	...	24	34	32	25
Bone ash	..	28	30	35	40

Add about 0.05 per cent of good blue stain. The biscuit firing is done between 1100-1200°C. Very careful control is necessary as slight over firing causes the bone ash to decompose evolving gases which deform the wares.

Most of the modern potters use felspar in place of Cornish stone, as the latter always varies in composition.

China clay	...	35	33	30	40
Felspar	...	25	47	47	12
Bone ash	...	40	20	20	40
Quartz	...	—	—	3	8

In some old recipes for china of very good quality, a special frit is used in the body mixture.

Frit together :—

Felspar	60
Borax	25
Nitre	5
Salammoniac	10

Body mixtures.

Frit	45	35
China clay	40	35
Bone ash	15	30

The biscuit firing is done between cones 3 and 6.

The glazes used on bone china are generally fritted although raw glazes were used in older days. The same glaze does not suit for all bodies and the glaze which appears fine on one body may seem defective and craze on another.

The following are some typical recipes for china glazes. The recipes may be changed slightly to suit any particular body.

1. Frit together.

Borax	...	40
Whiting	...	10
Flint	...	20
Felspar	...	30

2. Frit together.

Borax	30
Chalk	20
Flint	15
China clay	10
Cornish stone	25

Glaze mixture.

Frit (1)	...	50
White lead	...	15
China clay	...	10
Felspar	...	15
Flint	...	10

Glaze mixture.

Frit (2)	...	65
Stone	...	15
Flint	...	10
White lead	...	10

In some old recipes common glass was used in the frit mixture.

3. *Frit mixture.*

Glass	... 69
Litharge	... 18
Nitre	... 8
Arsenic	... 4
Blue calx...	1

Glaze mixture.

Frit (3)	... 6
Flint	... 14
White lead	... 54
Cornish stone	26

4. *Frit mixture.*

Borax	... 13
Flint	... 87

Glaze mixture.

Frit (4)	... 30
White lead	39
Stone	... 30
Blue calx	... 1

The glazing temperature is much lower than that of biscuit firing and varies between 1000°C to 1100°C. Due to this low temperature of glazing, china ware can be decorated with underglaze colours of various delicate shades which is not possible with hard porcelain wares.

Parian Porcelain. These are mainly used for dolls and busts and left without a glaze. The following are some compositions of Parian bodies or biscuit porcelain.

	1	2	3	4	5
Kaolin	37	35	36	50	50
Felspar	63	45	60	47.5	36
Pegmatite ...	—	20	—	—	—
Flint glass ...	—	—	4	2	—
Quartz	—	—	—	—	10
Zinc oxide ...	—	—	—	0.5	1
Marble	—	—	—	—	3

Masses 1, 2, & 3 are used for small toys, made by casting, as the bodies are rather lean. They mature between cones 3 and 4. Masses 4 & 5 are quite plastic and workable by every method. The bodies after firing are very white. The firing temperature is between cones 8 and 9 under oxidising condition. If fired under reducing condition specially in the later stage, small bubbles or even bloating may occur.

Burning. One of the most troublesome parts of a potters job is to place the wares inside the saggars. Unless they are properly placed, they would stick to the sides of the saggars or to one another when the glaze begins to melt. To avoid this difficulty each article is placed on a special support made of refractory clays and known as *bumsen* in Germany. All round articles are placed on bumsen made of the same mass as that of the wares themselves so that the round edges may not get out of shape due to unequal contraction of different masses. The sides of contact between the bumsen and the wares are smeared with fine sand and oil to avoid sticking. Articles that are to be kept perfectly flat are placed on special bats previously fired and levelled on sand stone. Pipes and long cylindrical wares are generally kept hanging inside the saggars from strong refractory rods, and there are numerous other devices to suit particular purposes.

The manner of charging or filling up the oven is also very important regarding the nature of the wares to be placed in different parts of the oven. The first ring or the place next to the fire bags being the hottest

part of the oven, it is advisable not to place any delicate article there, which may get damaged by over firing. The manner of setting out the bungs of saggars is particularly important in down-draught ovens. Unless this is done properly, the heated gases may find an easier passage in one quarter than the others, and consequently this quarter will be fired up in advance of the others. The aim in setting out and building up the saggars should be, a regular spacing throughout and it should never be forgotten that the spaces between the bungs of saggars are the actual down-flues in down-draught ovens.

The method of forming a space under the bottom saggars is worthy of a little care, as this has an important bearing on the distribution of the hot gases. The best way is to use special bottom saggars supported on three legs, made extra strong to bear the whole weight of the saggars above them. This prevents the accidental blocking of any of the down-flues formed between the bungs of saggars and also on the floor of the oven.

The most common kiln for firing continental hard porcelain, is a two-chambered down-draught one described in chapter X.

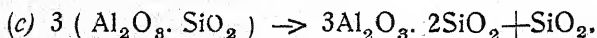
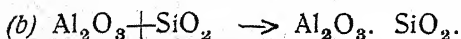
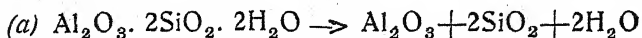
The heat balance of such an oven may be summed up as follows :—

Glost firing	16 per cent.
Biscuit firing	4 " "
Lost in ash	10 " "
Lost through chimney	...	30-35	" "
Other losses	...	30-35	" "

The firing of porcelain can be conveniently divided into three main stages.

Fore fire. This stage goes up to about 600°C and takes about 5-6 hours only, as porcelain bodies are very open, and the mechanical water is very easily driven out.

Middle fire stage is between 600°C to about 1100°C or just before the glaze begins to melt, and the time taken is about 10 to 12 hours. The rate of firing is slow at this stage, as the chemically combined water takes longer time to disappear. At the beginning of this stage the clay substance in the body begins to decompose into free oxides and afterwards unite to form sillimanite and mullite.



Sharp fire. This stage begins at the end of the second stage when the rate of firing can be augmented according to the nature of the wares. The felspar now begins to melt and dissolve the free quartz forming a viscous glassy liquid which softens more and more as the temperature rises, and which on cooling forms crystalline mullite interwoven in a glassy structure. The total period of firing a porcelain oven up to a temperature of 1400°C does not take more than 30 hours in all.

The cooling should be done very slowly and the oven door should not be opened before atleast 10 hours after the firing has been finished. Time taken by three men for discharging an oven (60 cu. meters) is about 5 hours, but nearly double the time is spent in charging the same.

The atmosphere inside the kiln, nearly up to the end of the second stage has to be kept oxidising in order to burn away any carbon or carbonaceous matter present in the body but it is safer to make it alternately oxidising and reducing, during the latter part of this stage. From this time the atmosphere must be kept reducing in order to avoid an unpleasant yellow colour due to ferric iron, which is replaced in a reducing atmosphere by a slightly bluish colour so much appreciated in porcelains. This reducing condition would not be difficult if there were no risk of hydrocarbons depositing on the wares which would be incorporated in the glaze during its vitrification and would give the wares a smoky appearance. This is avoided by *washing* up the kiln, whenever there is an accumulation of smoke inside, by making the fire oxidising to burn off the deposited carbon.

It is essential that the pressure inside the kiln should be a little more than that outside it, to prevent any air leaking through the cracks in the walls which open out when the oven gets heated. The first part of the cooling should be in a reducing condition until the glaze is solidified, after which the atmosphere may be neutral, and below 800°C it may be oxidising.

After firing, the articles are sorted and the defective pieces picked out. Sand adhering to the wares are rubbed off and small flecks on the glaze polished on the wheels, first with an emery stone and then on a rapidly rotating wooden wheel. Wares, the feet of which are slightly out of shape, as well as all flat articles, are rubbed on rotating sandstone with a little sand and water.

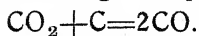
Defects. The chief defects that arise during the course of manufacture are :—

(1) Numerous pinholes on the glaze surface.

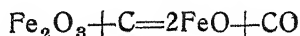
After the slow fire, if the oven is not cleaned out of its smoke properly, and the sharp fire begins too quickly, the smoke or carbon absorbed by the glaze explodes too late to be filled up by the mobility of the glaze. This defect may also arise as already mentioned, if the dust, deposited on the wares during the period of drying, is not properly cleaned before the wares are dipped into the glaze liquid.

(2) Big boils or abscesses on the surface of the wares after firing.

These are caused by the absorption of gases CO_2 , etc. by the body during firing, and when with the rise of temperature under reducing condition, these gases are expelled with great violence, they generally leave the wares with small swellings like pox marks.



Sometimes impurities present in the mass may cause boils but they often leave black spots inside the holes.



(3) Black spots on the glaze.

It is interesting to note that fragments of old moulds often leave black specks on the glaze, but chips from fresh plaster moulds melt to a green glass. It might be that alkalies and other soluble matter present in clays and partly absorbed by the working moulds, cause these black spots, but during his trials, the author could not produce the same defect by mixing suitable soluble salts with fresh plaster of Paris. The trials came out with different shades of dark grey colour but never with dark black as often seen on wares during natural course of manufacture.

(4) Deformed wares.

These may be caused by, uneven wooden boards on which the wares are dried before firing or defective placing inside the saggars; bad bumsen, or bending down the bottom of the saggars during firing.

(5) Cracking at the joints.

This is caused by unequal contraction of different parts specially if they are made by different processes. Whenever possible these parts should be joined by the glaze slip and not by any clay mass.

(6) Flecks of sand or iron.

These are caused by small bits of saggardust falling on the wares and can be easily avoided by cleaning the lower bottom of the saggars with a brush while stacking the saggars one above other and also by coating the bottoms with a thin glaze so that no sand can accumulate there. These flecks are polished off on

an emery wheel and then brushed with a mixture of glaze and dextrin, or glaze and tannin, and fired again. The latter mixture is specially suitable for bigger flecks or any dry spot on the glaze surface which often occur on big articles due to carelessness of the dippers.

(7) Cracks on the wares.

These may be caused during firing, if the firing is too rapid, and also if the oven, after firing is finished, is cooled too quickly. If the crack is caused during firing up, the edges of the crack will get rounded up by the molten glaze but when the crack develops during cooling down of the oven, the edges remain sharp. These cracks are repaired, when possible, by filling up the cracks with a mixture of glaze and fine sand, previously baked and finely powdered. The articles are then fired again.

(8) Lamination cracks.

When this appears in a fired article, there is likelihood of mistaking it for a heat crack. In insulators a crack of this nature produces mechanical weakness inspite of the body composition being perfect. Its nature is always to circle or to travel in grooves or petticoats of the insulators. Sometimes it appears in holes of insulators like a spiral spring slightly stretched as to produce a distortion. In a manufacturing concern it is very difficult to trace and locate the fault. Just like certain meandering rivers where we can find their origins but they suddenly disappear from our sight and finally see them emptying into a sea, this fault originates in one place, disappears and then reappears.

This originates near the extrusion press, not traceable during turning or glazing, develops in the kiln and reappears in the sorting section. This can be distinguished from a heat crack in the following way. (i) if the crack shows rounded edge too rapid firing at the commencement may be suspected, (ii) if the crack is produced during cooling, it will usually show no rounding at the edge of the crack, and if broken, the surface of the crack will be quite smooth, (iii) if the crack was in existence before firing commenced, the fracture will generally be much rough. So the rough fracture and rounded edges distinguish the lamination crack from the heat crack.

CHAPTER VI.

STONE WARES.

Stonewares, are opaque specimens of pottery impermeable to most liquids and specially to water. They are generally made of fire clays, but some modern specimens are made from white burning clays, with a hard felspathic glaze. The common or coloured varieties are generally coated with a salt glaze.

It is very difficult or rather impossible to put a line of demarcation between porcelains and fine stone wares. A thin piece of fine stone ware generally shows a little translucency, whereas a piece of hard porcelain when thick, loses its translucency completely. On the other hand, the impermeability is also not a satisfactory criterion to distinguish stone wares from ordinary *earthenwares*, for articles like drain pipes which fall under the stone ware group are not quite impermeable before they are glazed.

From the ceramic point of view, it is convenient to call as stonewares, all pottery, having a vitrified opaque body and almost devoid of porosity or permeability. The maximum porosity allowed under this group is 3 per cent only.

Stonewares can be divided into two main groups according to the nature of raw materials used for making them.

Fine Stone Wares, comprise the sanitary wares, domestic wares and the acid proof wares for chemical industries. Clays used in making these articles are generally purified before use.

Coarse Stone Wares are made from unwashed natural clays and denote the drain pipes and the vitrified tiles used for different purposes.

Sanitary Wares are now-a-days made from bodies much resembling porcelain bodies, but in older days they were mostly made of low grade fire clays or marls with a white coating on the surface to cover the coloured body. Even now some manufacturers use local marls for this purpose, and coat the surface with a white opaque glaze.

Bodies used for making sanitary wares differ greatly at different places but the aim of all the manufacturers is to build up a body that would vitrify to a dense mass below 1300°C and take a hard leadless glaze which should not craze during the use of the articles. The composition of such bodies generally lies between the limit of :

Clay substance	...	40 to 55
Quartz	42 to 55
Felspar	3 to 15

The firing temperature ranges between cones 5 and 10.

The following are the formulas for some continental and English stone ware bodies.

		1	2	3	4	5	6
Plastic clays	...	43	30	18	36	25	30
Kaolin	...	24	22	43	30	31	40
Quartz (calcined)	...	23	36	24	30	39	16
Cornish stone	...	10	12	15	—	—	—
Felspar	...	—	—	—	4	5	14

Bodies 1 to 3 are English and the rest of German origin. The body no. 5 was used by Seger for a long time for making stone wares.

A transparent, clear and brilliant glaze maturing between cones 7-9 is computed from.

Potash 0.3

Lime 0.4 0.4 Alumina. 3.5 Silica.

Baryta 0.3

The silica can be increased to 4 molecules but not further as otherwise the glaze would tend to devitrify in the lower part of the oven, that is, where the temperature is lower. On the other hand, if the alumina is lowered even by 0.02 equivalent, the glaze would begin to show milkiness at cone 7. It is advisable not to use less than 0.3 equivalent of potash. Magnesia acts as a basic flux in glazes rich in silica but baryta gives better results. This glaze gives very good results with underglaze colours and can be made up from.

Felspar	166
Sand	90
Witherite	59
Marble	40
Kaolin	25

A more plastic body used for wares with complicated shapes can be made from the following mixtures ;—

Plastic clay	...	58	45	33
Kaolin	...	—	7	17
Quartz	...	25	26	25
Felspar	...	17	22	25

A felspathic glaze suitable for these bodies and maturing at cone 4 has the following composition :

0.3 K_2O			
0.5 CaO			
0.1 MgO	0.4 Al_2O_3	3.85 SiO_2	
0.1 BaO			

This glaze can be computed from :

Felspar	167.0
Sand	111.0
Marble	50.0
Kaolin	25.8
Witherite	19.7
Magnesite	8.4

The mass is prepared in the same way as already described for that of porcelain, but the wares, since they are made thick, are dried very slowly and carefully to avoid any drying cracks. Occasionally they are glazed in the green condition but often fired biscuit and then glazed and fired again. The glaze may be made opaque by the addition of zinc oxide and tin oxide, or it may be coloured by common colouring agents.

Some compositions of stone ware bodies using Indian materials are given below.

	1	2	3	4	5
Rajmahal kaolin ...	—	—	—	30	30
Magma fire clay ...	60	—	—	—	25
Nalhathi fire clay ...	—	60	55	20	—
Mihijam felspar ...	20	28	25	30	25
Mihijam quartz ...	18	10	19.5	20	20
Marble powder ...	2	2	1.5	—	—

All these bodies when fired at 1160°C have porosity less than 3 per cent. Bodies 1 to 3 have cream colour and should be covered with a white opaque glaze. Bodies 4 and 5 are quite white.

A suitable glaze for the above bodies maturing at 1160°C can be composed of ;—

Felspar	45
Quartz	25
Kaolin	10
Marble	10
Zinc oxide	10
				<u>100</u>

Heavy sanitary wares like laboratory sinks and wash basins are often made from vitrifiable clays and grog. The composition is rather simple. Fifty to sixty parts of a good vitrifiable clay are mixed with forty to fifty parts of grogs and made into casting slip with suitable electrolytes. The ratio of clay and grog should be so adjusted that the total shrinkage of the body does not exceed 4 per cent. A greater shrinkage may cause

cracks specially at the bends and joints. The grog used should be properly graded for the adjustment of the shrinkage. A mixture of fine and coarse grog produces less shrinkage than equal amount of coarse grog only. The presence of fine grog produces better surface. The consistency of the slip should be about 36 ozs to the pint. The articles are then cast in thick plaster moulds. The cast articles are dried very slowly preferably in an underground cellar to avoid rapid and unequal drying. If there are very minute cracks in drying, they are not visible before the articles are fired. Hence great care is to be taken during the drying stage of these heavy articles. Sometimes these wares are pressed in moulds when the drying cracks are minimised but casting produces better articles.

As these grog bodies are often coloured, a white engobe is invariably used to cover the surface of the ware. The engobe is best applied by spraying when the articles are *leather hard*. After the engobe and the body have dried thoroughly, the articles are fired first time, generally between temperatures 1100°C to 1160°C .

An engobe for such bodies can be prepared from the following composition.

Rajmahal kaolin	45
Flespar Ajmere	30
Quartz	23
Marble	2

100

A suitable glaze for this engobe maturing at cone 04 can be made from the following.

<i>Frit mixture.</i>			<i>Glaze mixture.</i>		
Red lead	...	20	Frit	...	80
Borax	...	22	Kaolin	...	8
Felspar	...	17	Quartz	...	6
Quartz	...	30	Tin oxide	...	6
Marble	...	11			
<hr/>			<hr/>		
100			100		

Some modern sanitary wares are covered with lightly coloured enamel glazes. Some compositions of coloured enamel glazes are given below.

1. A light bluish pink coloured enamel glaze maturing between cone 5 and 6 can be prepared from the following composition :—

0.4 PbO		
0.2 K ₂ O		
0.2 CaO	0.3 Al ₂ O ₃	3.0 SiO ₂
0.2 ZnO.		

Add to the mill batch tin oxide 3 per cent, zirconium oxide 3 per cent and orchid stain 5 per cent.

The stain is prepared by calcining at cone 10 the following mixture :—

Tin oxide	86
Borax	8.6
Potash dichromate	5.4
			<hr/>
			100.0

2. A light yellowish brown glaze maturing at about 1200°C can be made up from the following composition.

Potash felspar	30
Plastic clay	6
Quartz	25
Whiting	6
White lead	28
Zinc oxide	5
			<hr/>
			100

Add to the main batch Tin oxide 6 per cent and Sodium Uranate 1.4 per cent.

Often one to two per cent of borax or boric acid are added in the mill which intensifies the colour and improves the gloss. These enamel glazes are best applied by spraying through a fish tail spray gun at a pressure of 45 lbs. per sq. inch. The consistency of the glaze slip should be made at 30 ozs. per pint.

Chemical wares, as well as domestic utensils, are made from siliceous vitrifiable clays, and they are included in the first group as the clays are generally purified before use, unless the natural clay is so homogeneous and free from grits that it requires no further purification or mixing.

These secondary clays contain as impurities, small amounts of Na_2O , CaO , MgO , TiO_2 and Fe_2O_3 . These oxides influence the temperature of the glassy formation as well as the viscosity of the glassy melt. When the clay is heated to about 1000°C the alumina and silica begin to combine to form mullite. Mc Vay and

Thomson (1928) obtained definite patterns of mullite from a sample of clay heated slowly to 950°C. The amount of mullite increased gradually with an increase of temperature or the mullite became better crystallised. With the further rise of temperature the fluxes melt and bind the crystals and amorphous mullite with a glassy cement. If there is too much silica in the clay, the cement becomes brittle which lowers the thermal endurance of the product. Stone ware vessels meant for heating purpose should have good heat conductivity. In this respect CaO and Na₂O are more helpful than K₂O. Hence stone wares made from impurer clays often have greater heat conductivity than porcelains made from purer clays.

The vitrifiable clays which are specially suitable for acid proof chemical wares are those which yield an impervious mass when heated to a temperature between 1150°C and 1300°C, but do not lose their shape when heated to a higher temperature. If the clays are not sufficiently heat-resisting, the slow heating in a large kiln has a tendency to cause collapse of large vessels. Clays which contain about 6 per cent of natural fluxing materials, usually give the best results and with larger amount of fluxes, the margin of safety of firing becomes less.

As the naturally suitable clays are not common in all localities it is customary in many places to employ a more accessible clay, such as a low grade fire clay, and either heat it to the point of sufficient vitrification or mix it with a flux in order to produce a more readily

vitrifiable body. Under ordinary commercial conditions it is seldom advisable to add felspar, whiting or other materials of similar character, as it is very difficult to distribute the particles of these with sufficient uniformity through the clay mass. A preferable plan is to use a more fusible clay which can be mixed very uniformly. To obtain the best possible results it may be necessary to blunge either or both the clays with plenty of water, remove the coarse particles with a screen or sieve and then to separate the excess water in a filter press. It is not unusual, however, to treat the more fusible clay in this manner and then add to it the requisite quantity of ground fire clay.

One of the finest acid-proof materials found in the British Isles is a highly siliceous fire clay containing—

SiO_2	80
Al_2O_3	14
Fe_2O_3	4
CaO	1
Loss	1

The remarkable thing about this material is its low content of fluxes as ordinarily considered, but in this case the iron oxide is made to act as a flux by the conditions under which the material is burned. This material is chiefly suitable for the manufacture of small articles of simple forms but for larger vessels, such as acid jars, still heads, condensing coils etc., a more plastic clay must be employed.

The body used for acid-proof wares must, when burned have the following among its chief characteristics. It must be wholly impervious to water and should not yield more than 0.3 per cent of dissolved matter when boiled with the acid for which it is to be used. It should have a range of safety of about 300°C, and should not be unduly sensitive to sudden changes of temperature. It must have a high plasticity in order that it may be made into the relatively difficult shapes which are sometimes required, and it should not shrink by more than 8-9 per cent in both drying and burning.

The chemical analysis of an extensively used stone-ware clay of Germany has the following composition—A.

			A	B	C
SiO ₂	70.12	58.02	56.95
Al ₂ O ₃	21.43	27.95	28.51
Fe ₂ O ₃	0.77	—	—
MgO	0.39	0.56	0.29
CaO	—	1.65	1.37
Alkalies	2.62	2.42	1.43
Loss	4.92	6.85	8.25

Clays B and C are Indian fire clays the first from Magma in Behar and the second from Ranigunj in Bengal. These clays are highly plastic and require no preliminary purification.

The preparation of the body from materials chosen with regard to what has just been said is similar to that of ordinary products. For the best wares, it is well to

take the cakes from the filter press in a rather soft condition and to keep them in a cool place for a month or more in order that they may season properly. After this they are passed through the pugmill. An alternative method which is cheaper but less satisfactory consists in reducing the hard dried clay to a powder in an edge runner mill passing the ground clay through a screen to remove the coarser particles, and then mixing it with water in an open trough mixer, and finally compressing it in a pugmill. Various modifications of these processes are used when several materials enter into the composition of the body.

In most works engaged in the manufacture of acid proof ware, the goods are produced by throwing and moulding. Throwing the ware on a potters wheel is the cheapest and the best when great accuracy of shape is not required, and where a few vessels of any one shape or size are produced at a time. Some of the more complex pieces must be made in separate parts, which are afterwards joined together. Where great accuracy of dimensions is required, the thrown articles may be turned on a lathe or finished by a modeller when they are in a half-dry state.

Moulding by hand is largely used for acid-proof ware, the pieces being made in plaster moulds. Usually two-piece moulds are employed, each half being filled with a bat or slab of the plastic body, which is beaten with the hand or a large pad so that it takes the shape of the mould. The two pieces of the mould are then fastened together and the clay pieces are joined with a

little soft paste by means of a stick or the hand as convenient according to the nature of the articles. The mould with the content is then set aside for a time, after which the article is removed and *finished* by another workman, who removes all surplus material and makes good any obvious defect.

When a thread is required in the neck or other parts of a vessel in order that a pipe or cap may be screwed into it this thread may be made in one of several ways. The usual method is to cut the thread while the article is in the mould by inserting a screw with a corresponding thread—an action precisely similar to screwing the cap on a bottle. Sometimes the first cutting is made with a somewhat rough screw, and the threades are then trimmed by passing in an accurately cut screw.

Extrusion is used for making pipes, condensing worms and similar pieces of acid-proof ware. This process is essentially the same as that used for making sanitary pipes and wire-cut bricks. When the pipes are required to be curved, as in condensing worms, this shape must be given to them by skillfully twisting the pipe as it comes from the machine, and receiving it on a rotating drum until the clay supports are attached. Sometimes these worms are made by building the coil up laboriously in section, but for this purpose a highly tenacious body is required.

Mechanical pressing is chiefly confined to the very small objects, such as caps etc. The well known screw presses are employed for this purpose and the body is

made leaner by the addition of suitable amount of fine grog.

The method of casting was used to a very limited extent with this class of ware. In fact, casting of large pieces with clay slips containing but little water, in suitable plaster moulds, has only been tried a few years ; and it has been shown that the large pieces made by casting are very often superior in quality to hand work, and owing to the simplicity and cheapness of production considerable saving in the manufacture can be made.

In some cases the ware is covered with a *dip* or engobe of finer clay than that used for the goods as a whole, and often coloured suitably, but this is not necessary if the body has been well composed.

The ware is dried in the usual way, care being taken to avoid too rapid a drying, especially of projecting portions and spigots.

The wares are mostly salt glazed in common draught kilns. The ware must be placed in the kiln in such a manner that the salt vapour evolved from the fire places may have access to every portion of the ware which it is desired to glaze.

Fusible glazes are also used in place of salt glaze though the latter is cheap and very effective. Dipped glazes for this purpose are made from blast furnace slags, or from a mixture of cinders, lime, and sand, which are quite satisfactory in most cases. A lead glaze should not be used, as it does not adhere sufficiently well to the body and is more readily attacked by acids.

Drain pipes are made either from a vitrifiable clay mixed with sand and grog, or from low grade fire clays. Clays used for these articles are not washed or purified but worked out just as they come from the pits, except in some cases where weathering seems to improve the clay to a great extent.

The mass is prepared by grinding suitable proportions of clay and grog together, say, two thirds vitrifiable clay and one third fine grog and sand, in pan roller, and then mixing the same in a mixer where water is added from a tap. It is advisable to keep this wet mass in a cool place for some days for maturing and then to pug it thoroughly, before the mass is used for pressing.

Drain pipes are generally made in special pipe presses, and as it is essential that the goods should not get out of shape by their own weight, the pressing must be done vertically. Pipes of diameter ranging between 2 inches to 18 inches are made in common belt driven presses but for larger ones machines with direct steam pressure should be used. Elbows, junctions etc. are better made in plaster moulds.

When the pipes are sufficiently stiff, they are fettled and the defective parts touched up by hand while the pipes are revolving on a wheel. The spigot ends of the pipes are also scratched at this stage so as to increase the adherence of the mortar or cement. The pipes are then placed on the drying sheds generally erected round the top of the kilns to utilise the waste heat. These pipes take 3-5 days for drying.

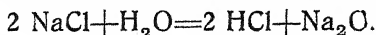
Sewer pipes are set with the spigot end down and the larger sizes are placed on rings of green ware to take up the shrinkage strain. The setting is in a series of circles. Cranes are used for handling large sizes. The spaces between the bags are filled with small sizes, three to four lengths high. Then come rings of intermediate sizes and afterwards the large ones which should not be set next to the bags or even in the second ring where they would be within the variable influence of high temperatures. The setting height is usually four standard lengths or their equivalent in longer lengths. The setting is such that the sockets are in touch which secures the stability of the columns of large pipes. Smaller sizes are set inside the larger ones, but there must be sufficient difference in size to insure a clear annular space between the two, otherwise the inside of one and the outside of the other will not have a good glaze.

Elbows, branches, tees, traps etc. are largely set on top. Tees and branches may be set in the regular columns, but elbows, traps etc. must be set on top. In various simple ways the top of the kiln may be set with special forms, often without any bracing; but unstable pieces may be braced, one against another, by clots and strips of clay.

Pipes are usually burned in round down-draught kilns.

Salt glazing. A salt glaze is merely a soda-silica-alumina glass coating on the surface of the ware. Salt is used for its abundance and cheapness. It fuses and

volatilises at a moderately low temperature (820°C) and does not change chemically in fusion or volatilization. Water is necessary for the decomposition of the salt and the reaction is as follows :—



The limits of the ratio of alumina to silica within which a good glaze is possible as determined by Barringer, are, one alumina to 4.6 silica for the minimum, and one alumina to 12.5 silica for the maximum. A highly aluminous clay does not take up the salt vapour easily at the usual temperatures of firing whereas a highly siliceous clay produces a glaze which is easily attackable by acids or water.

The best glazing temperature is not yet definitely determined, but experience has found out that temperatures between cones 3 and 8 are quite satisfactory. The salting period varies from 3 to 24 hours and the quantity of salt required varies accordingly.

The salt not only acts on the goods, but also on the walls of the kilns, and rapidly destroys them, if care has not been taken to employ sufficiently aluminous bricks in which little or no silica is found in free state or to wash the inside of the kiln with an aluminous clay every time before firing.

The process of firing salt glazed pipes can be divided into five distinct periods, although each period more or less overlaps the next one.

Water smoking is one of the most troublesome periods and is of much importance to the manufacture of the larger sizes and double strength sewer pipes.

The period covers the time from the start until the ware has given up all the mechanically combined water. A temperature of about 150°C would be obtained during this period. The time of water smoking varies from 24 to 96 hours, according to the size of the ware or nature of clay used. A few of the effects of too rapid water smoking are, scaling or blowing, blistering, and cracked sockets.

In down-draught kilns, the pipes on the bottom are subjected to greater humidity or dampness, and we find on the bottom rows of pipes, the largest percentage of blisters. Cracked sockets is a common trouble when using excessive draught during water smoking. Too rapid firing at the beginning will cause trouble with top pipes, too slow beginning followed by too rapid firing causes the trouble to occur on the bottom pipes, and many times it is necessary to increase the stack draught at the beginning, by starting fires in the stack to warm it.

Heating up stage, covers the time from water smoking to oxidation. This period ranges from 150°C to 450°C and if special attention is given by the fireman, the temperature during this period can be raised rapidly. This period generally lasts from 20 to 30 hours.

Oxidation, period is of great importance for the successful burning of clays high in carbon content. Incomplete oxidation is very injurious to pipes giving them a spongy interior, distorted shapes, and inferior ring. The best way of judging the progress of oxidation is by drawing trials periodically until the interior of the

trials are free from carbon. The draw trials are placed near the door of the kiln so that on removing some of the bricks the trials can be easily taken out. The trials should be drawn at regular intervals after the kiln attained a temperature of about 550°C . The duration of this period is about 80 to 90 hours until the kiln has an average temperature of about 800°C .

Vitrification period, follows close upon oxidation and if the oxidation is not completed before vitrification starts, there is little chance for its completion afterwards, for when a thin layer of clay vitrifies on the surface of the ware, no air can penetrate to the imprisoned carbon. As the temperature increases the carbon burns inside the clay body, and as it must have oxygen for the combustion, to form carbon monoxide, the oxygen is taken from surrounding particles containing it. This gas being imprisoned in the intensely hot clay ware, which has almost reached a molten stage, will cause it to swell or bloat and then we have the spongy interior and distorted shapes.

The vitrification period covers two important steps. Raising of the required temperature within a reasonable time, and making uniform distribution of heat over the entire kiln. The average time for vitrification is about 36 hours, starting at about 800°C and going up to about 1160°C . This time will vary considerably due to different kinds of coal, amount of draught, size and number of fire boxes and to the nature of the clay.

In raising the heat too fast, the necessary amount of air is not admitted for proper vitrification. Quick

firing promotes reducing condition, the heat remaining in the top part, burning the top pipes and the outside rings of pipes too hard and causing the *fillings* or *stuffings*, that is the small pipes inside larger ones, to remain too soft. When glazing the ware in this condition the top pipes may be very nice while the bottom ones, and the stuffings remain practically unglazed. By regulating the draught and leaving fires open, a soaking process is obtained, which distributes the heat uniformly throughout. The soaking process should begin as soon as the temperature and vitrification of the top pipes are sufficient for glazing. No large amount of heat should be lost during the soaking period, for once lost it is very difficult to regain it. When the soaking process is on, the draught is reduced to check the inrush of cold air, and by giving close attention to fires while the air is going in over them, the temperature can be held constant, and the heat conveyed from the fires to the bottom or floor of the kiln.

Salting. After the vitrification has set in and the trials show reasonable hardness, the kiln must be prepared for salting in the following way. The fire-holes must be thoroughly cleaned, the best plan is to clean alternate fireholes to avoid cooling down of one section of oven and the resulting heavy smoke. The fire is allowed to burn until the fresh charge is aflame and the volatile matter is expelled. This ordinarily requires about 15 to 20 minutes with long flamed coals and a little less with short flamed ones. At this stage the fires are at their greatest intensity. The salt

is now applied in small amount at a time and well spread over the fire, as larger amount would deaden the fire and remain unburnt. A period of about ten minutes or so is now allowed until the salt decrepitates completely, and then another round is applied as stated, followed by a small amount of coal or the closing of the fire doors. When the third round is applied and salt burned, another light fire is put on. Allowing time for the volatile matter to be driven off, three more rounds are applied. Trials can be drawn after every three rounds to determine the progress of the glazing. The fires should be shaken or given a light cleaning after every three salt applications. As the salting progresses, the ware continues to harden, since the salt fumes have a fluxing action. Six rounds of salting should be sufficient to develop a good glaze in most cases but some clays are very difficult to glaze and require some more rounds for the proper development of the glaze.

The action of salt glazing is heat absorbing or endothermic, so it is necessary to add a little fresh fuel with each charge of salt in order to keep the kiln temperature uniform. Cold air should never be admitted over the fire except in cases where a kiln has extremely poor draught and conditions are very reducing. The admission of cold air over the fire-bed has the effect of reducing its temperature, and thus cutting down its efficiency so far as volatilizing the salt is concerned. For best results all air must be admitted through the fuel bed, and not over it.

Cleaning and stirring of the fires are necessary during this operation. It will be noted in this connection that the salt to a certain extent melts and combines with the coal ash to form a soft glassy slag which runs down through the fuel bed or grates as the case may be, hardens as soon as the cool air strikes it, and prevents the air from entering. Hence it is of vital importance that the coal bed be shaken often to break this formation of hard slag.

The amount of salt used or coal consumed vary to a great extent according to the nature of the clay, used and the design of the kiln. As a very rough guide however, consumption of more than 20 lbs. of salt and 250 lbs. of good coal per ton of pipe should not be permitted without thorough investigation that larger quantities are unavoidable in that particular case. Salting period varies from 5 to 25 hours, but 6 hours is common in majority of cases.

The colour of a salt glaze is affected by the character of the kiln atmosphere as well as by the composition of the body. The natural colour of a salt glaze is golden yellow. Under reducing conditions it absorbs carbon and the colour darkens to a brown or even to a dull black. If the body is dark, as a shale pipe the colour of the pipe surface is correspondingly dark due to the dark back ground. Sometimes trade demands coloured ware, and this can be produced at will by the process commonly known as *flashing*. The process consists in producing a thin coat of smoke on the surface of the ware and then washing out the excess carbon by

oxidising atmosphere, leaving only those that penetrated the pores of the ware. Then another skin of smoke is produced and washed out in the same manner. This alternate reducing and oxidising conditions leave the iron on the surface in a reddish condition and when the glaze is applied on it with a bright oxidising fire, a cherry red to dark brown colouration may be obtained according to the skill of the fireman.

Defects. Numerous difficulties have to be encountered and overcome for a successful firing and these must be thoroughly understood by the technical man.

Blowing or slabbing occurs in the water smoking period and is said to be caused by the development of steam, the pressure of which forces off large chips from the surface of the ware. The trouble can also be traced back to the press work caused by lamination planes in the ware due to defective making, which afterwards are forced out by the pressure of the steam or gases evolved within the body.

Blisters in burned pipes are often due to the gases given off by pyrite or other minerals, which cannot escape in consequence of the vitrification of the surface of the wares, but under advanced heat the gas volume increases with great pressure and cause blisters.

Pimples or rough surface, are due to the reduction of the iron compounds on or near the surface of the ware and their combination with silica by fusion. The fused particles naturally assume globular forms projecting from the surface of the wares. Wares that pimple badly should be subjected to alternating reducing and

oxidising conditions until the globules have been fully developed and absorbed.

Cracking of the ware is caused by too rapid heating up during the water smoking, which would tend to develop fine drying cracks on the surface and near the sockets. These cracks would not heal up in the burning nor be covered by the glaze.

Crazing of the glaze is due to too rapid cooling specially if the body does not suit the glaze. Where the glaze is liable to crazing, it is very important that the ware should be carefully cooled in order to get a maximum annealing and if possible, the best plan is to modify the body. Clays containing high alumina are liable to craze. Mixing of free sand with such clays would cure crazing.

Smoked ware has a lustreless gunmetal like black appearance, due to excessive absorption of carbon by the glaze. Sulphur gases have also some influence for the dullness of the glaze.

A white scum sometimes appears on the ware after it has been in the open for a short time. This is due to excess salt fumes in the kiln atmosphere which were deposited on the ware. As a matter of course, the first heavy rain will remove the scum from the ware but in order to avoid its formaton, a light fire should be applied after the salting has been completed and at the same time the stack damper should be raised high to increase the draught and draw the salt fumes from the kiln.

The chief test for pipes is to ascertain their resistance to pressure by the help of a force pump or by means of a hydraulic accumulator. The pipes to be tested should be exactly filled with water, the pressure being gradually and not suddenly applied. The test may be made either on a single pipe or on several pipes joined together.

Vitrified tiles. Stone ware tiles are generally made from vitrifiable clays but often a fusible clay is also used in conjunction with a more refractory one. They are generally made of one colour but sometimes different patterns are impressed on them as in the case of *encaustic tiles*. In special cases when white paving tiles are required, they are made from white burning clays mixed with stone and flint.

The body is prepared by mixing different proportions of suitable clays and grinding them in panroller or edgerunner mills. The ground mass is then put in a mixer where water and suitable colouring matter are added. The mixed clay is then put in a horizontal pug mill, from where it is taken in lumps by boys and dried in specially constructed driers, generally in the form of tunnel heated by coal or waste heat from other furnaces.

The dried blocks of clay are then carried to the disintegraters where they are powdered sufficiently fine to pass through no. 25 lawn. Too much fine powder is not suitable for dust pressing. The dust generally contain about 5 to 6 per cent of moisture, water being added if necessary, before the clay is powdered, as it is

not very easy to mix water properly with powdered mass. The dust is stored in separate rooms according to their respective colour and taken to the press house when required.

The moulding of the tiles is done by pressing the powder into the respective shape. Clay powder being loose and containing more or less air the pressing under full pressure cannot take place in one single stroke. The air enclosed in the powder would render the tile loose and slatelike, thus setting up a tile with an open texture and making it absolutely useless. To avoid this trouble the initial pressure has to be followed by a pause in the pressing, during which the escape of the air may be distinctly felt. A strong second pressure will close up the texture of the tile thus giving it the tightness and the required strength. Proper escape of the air is a point of extreme importance. It depends essentially, besides on the working and design of the press and the die, on the kind of the powder. A powder very finely ground contains more air, needs a considerable filling-height in the die and very often forms laminated tiles. Moreover, its manufacture is more expensive, its use on account of the dust created in the workshop is more disagreeable than that of materials composed of coarse grits, like the powder delivered by the edgerunner mills.

Tiles from pulverised clay are made on hand spindle press, friction spindle press, and by hydraulic press. The first one is as a rule, used for the manufacture of borders and profiled pieces, as their small output and

tedious handling make them unfit for making as normal tiles. Hydraulic presses are suitable in large works only, whereas in small works, friction spindle presses are practically, the only type in use on account of their simplicity, high output and small amount of capital outlay.

Messrs Dorst & Co. have patented a friction tile-press which has an output from 600 to 700 first class tiles of standard size (6"X6"), per hour, requiring the attendance of one man and without any further assistance. This press is fitted up with an electrical heating equipment to warm the dies so that the disadvantage of sticking of the pressed tiles to the dies is avoided.

Encaustic or inlaid tiles. These are made by pressing different coloured powders in a manner to produce different designs on the tile surface. The coloured powder is generally made a little more fusible than the common body in order to have a firm grip with the latter. Different coloured dusts are applied on the tiles in an ingenious way. A templet about one twentieth inch thick formed of bands of copper soldered together forming cells having the shape of the designs, is filled with the definite coloured powder into the proper cells. The templet thus filled is placed in the bottom of the press box, a slight pressure is given to it, and the mould is then filled with the common body, the whole being then compressed under a powerful press.

The tiles are generally sent to the fire without previous drying but the water-smoking period is prolonged

on this account to about 100 hours. Round down draught kilns are generally used but for larger manufacture continuous kilns are often employed. The total period of firing lasts to about 220 to 230 hours according to the nature of clay employed and the temperature of firing. Vitrified paving tiles are fired between cone 9 and 10 but for some fusible clays lower temperatures are also used.

Good vitrified tiles have a porosity below 4 per cent and they offer resistance to wear quite equal to that of hard natural stones.

CHAPTER VII.

EARTHENWARE.

The term earthenware denotes all porous pottery with a suitable glaze on the surface of the wares. The word is often misused to indicate common pottery sometimes without a glaze. Unglazed pottery made from common clay is known as *Terracotta*. Glazed earthenware are made nowadays both from white burning china clay or ball clay and from red or buff burning common clay. In order to make a clear distinction between these two types of glazed wares it is convenient to call the one as *fine earthenware* and the other as *common earthenware*. The glazes used on these two types of bodies also differ widely. Modern fine earthenware as made extensively in England are covered with an alkaline plumbiferous glaze generally fritted before use. These articles are very much suited for daily domestic use as the glaze is not affected by the contamination of our food stuff of any kind. The common earthenware are generally coated with a raw plumbiferous glaze which may be affected by dilute acids or alkalis. These wares are generally used as decorative household articles.

Fine earthenware as made in England with an almost white body and a similar semi-transparent glaze is generally superior to similar products of other countries. They are cheap in price and well suited

for daily domestic use. The raw materials used in composing this body are : china clay, ball clay, flint and Cornish stone. The china clay gives the whiteness whereas the ball clay gives the necessary plasticity which helps to a great extent for the quick production of the green articles and to the consequent cheapness of the product. The calcined flint gives the hardness and also whiteness to the ware and the Cornish stone serves as a flux.

The above named raw materials are finely ground and converted into liquid slip or slurry with water in separate blungers. In order that the subsequent mixing should be satisfactory, it is necessary that the slips should be made of the same consistency though not of equal density. For this purpose the following convention is generally followed in England though not so strictly in every factory.

Ball clay slips are so made that one pint weighs 24 ozs. China clay slips weigh 26 ozs, flint or quartz slips weigh 32 ozs and stone or felspar slips weigh 31-32 ozs.

The mixing of the ground materials is done in the wet condition. A definite volume of each kind of slip is run into a vertical tank called the mixing ark having a vertical shaft with paddles. This method of *wet mixing* is largely followed in England rather than in any other country. The advantage of this method is that the moisture contents of the raw materials specially the clays do not come into account when calculating the composition of the body mixture. The disadvan-

tage is that for each kind of slip a separate storage tank should be provided and the slip should be stirred to prevent the solid matter from settling down.

After mixing, the slip is sifted through a lawn ranging from 80 to 120 and passed through an electromagnet to remove any iron particles that may get mixed up with the mass during the previous operations. The slip is then pumped into the filter press. A more powerful pump is required to press a ball clay body through the filter cloths than the usual practice with porcelain bodies containing china clays only. If the clay slip is dried by slow heat the mass becomes more plastic and easier to handle. The pressed mass is then thoroughly pugged in a pug mill when it is ready for moulding. The modern vacuum pug mills have removed many after troubles and produce better wares.

Body Compositions. In countries other than England, quartz, felspar, pegmatite and whiting are often used in place of flint and Cornish stones. A few typical compositions of foreign earthenware bodies are given below.

	1	2	3	4	5	6
China clay. ...	10	35	25	50	24	25
Ball clay. ...	45	20	25	—	40	30
Flint. ...	35	32	34	30	25	30
Stone. ...	10	13	16	—	—	—
Felspar. ...	—	—	—	18	10	—
Pegmatite. ...	—	—	—	—	—	10
Whiting. ...	—	—	—	2	1	5

No. 1 is English cream earthenware; No. 2 is English white earthenware and No. 3 is English granite ware. Often 0.02 to 0.05 per cent of cobalt is used in these bodies to make them white. The best way of introducing this small amount of cobalt is in the form of its soluble salts which can be precipitated later by a small amount of ammonia. Nos 4-6 are continental earthenware bodies generally known as steingut, faience, majolica etc. The ball clay for these bodies is generally replaced by a plastic fire clay having low iron content. Calcined quartz is used for flint. Small amount of lime or whiting acts as a bleaching agent and makes the fired body whiter but more than 5 per cent of lime in a semivitreous body is not recommended as it tends to lower the firing range of the body. The fine earthenware bodies are generally fired biscuit between 1160°C to 1200°C and then glazed at a lower temperature, but the modern tendency is to mature the body and the glaze together so that there is less risk of crazing.

A few compositions of fine earthenware bodies from Indian materials are given below.

	1	2	3	4
Katni fire clay ...	—	40	—	—
Magma fire clay ...	30	—	—	—
Kaolin Raj mahal ...	20	15	48	45
Calcined quartz ...	32	30	34	36
Felspar Mihijam ...	13	15	16	15
Marble powder ...	5	—	2	4
	100	100	100	100

The fire clays used for this purpose should be carefully washed and the iron particles removed by magnet before use. The presence of these fire clays increases the plasticity of the body but invariably imparts slight cream colour which can be masked by proper amount of blue stain. The above bodies mature at about 1160°C.

In making wall tile bodies different mixtures are generally used. More of flint and less of stone are added in order to avoid crazing. A typical recipe of a tile body used in England is given below.

Ball clay	33.6
China clay	18.2
Flint	38.1
Stone...	10.1

The powder for pressing the tiles is made by drying the cake from the filter press in artificial driers [generally heated from the waste heat of kilns used for firing the wares. The dried cakes are then pulverised in edge runner mills sifted through lawns generally Nos. 20 to 40, when the dust is ready for the press. The moisture content of the dust varies from 6 to 9 per cent.

Sometimes fine earthenware bodies are coloured and sold under different names like, jasper, basalt, semian etc. A few compositions of these bodies are given below.

		1	2	3	4
Plastic clay	...	67	78	50	50
Calcined quartz.	...	10	15	—	30
Bone Ash	20	—	—	—
Barytes.	—	5	—	—
Felspar.	—	—	10	10
Cobalt Salt.	3	2	—	—
Haematite.	—	—	30	—
Manganese Oxide.	...	—	—	10	—
Thievier's earth.	...	—	—	—	10

No. 1. Skyblue jasper body. 2. Blue jasper. 3. Black basalt and 4. Semian red body. Fire at cone 3 to 4. In order to show the full colouring effect these bodies are not glazed but often decorated with designs in relief.

Moulding and shaping of the wares are done in the same ways as described in previous chapters. Throwing on the wheel and jollying are generally used for all round articles. Casting is the universal method for all complicated shapes.

Drying. After the goods are made, they are taken into the driers with the moulds. The driers are erected at the back of the working benches so that the workmen do not have to go far. The driers are heated by steam coils and generally kept at temperatures ranging between 30°C to 40°C. In large factories separate drying chambers are built as rapid drying requires a fairly hot atmosphere and if such driers are placed in the moulding shop, they would soon make

the atmosphere of the work room full with steam which is quite undesirable for the health of the workmen.

It is a common experience with the potters that sometimes wares come out of the drying chamber badly cracked. Different factors that are responsible for the drying cracks are summarised as follows.

1. Composition and consistency of the body. If the body is made of too much nonplastic material, it loses the binding power and cannot stand the strain during drying caused by the shrinkage of the clay. When too much water is added to the plastic body it is liable to crack during drying. If the clay is not made homogeneous by proper pugging it would crack in drying due to unequal shrinkage at different parts.

2. Defects arising from bad making. The clay lump should always be made to run to the top of the mould by hand before the tool is inserted, without leaving deep furrows or ridges caused by the fingers. The best results are obtained only when the tool leaves the piece shining all over but with no free water or slurry left on the surface of the clay piece. If the piece is finished too dry, its surface will be rough and open which condition naturally predisposes it to crack in drying. The speed of the jigger has also much to do for the cause of this fault. It is considered that a speed of 300 to 325 revolutions per minute is quite sufficient for straight cups etc. and for very thick articles. Slower speed would tend to drag the clay

instead of cutting it cleanly. When the profile is not strong enough, it shakes on the sticky clay and cause uneven pressure on the articles and lead to cracking on drying. Consistency of the plaster moulds also governs largely the nature of the cast piece.

3. Defects due to bad drying. The faults arising from inefficient drying, have been already discussed in Chap III.

After the articles are dried, they are polished or *fettled*, as it is called, with sand paper. Cups are boxed with one another face to face with gum so that they may retain their shape during firing. In boxing them the handles are placed on the same side. A gum for this purpose can be easily made by boiling dextrin in water with a little common gum or gelatine.

Chemical Compositions. Common pottery bodies are mixtures of many compounds derived from different minerals. Some of these like lime, magnesia and oxides of iron are stable at high temperatures, others like quartz and flint are inverted to different crystalline forms having the same chemical composition, but some compounds like kaolin and felspar break down at high temperatures. Common clay products are heated to a condition of partial fusion only. The main effects of heat needed for producing earthenware bodies are to harden the products sufficiently with some reduction of volume to produce a dense mass. The heating is not carried to such a temperature when the body may vitrify completely.

In order to guard against the deformation of the body near its fusion temperature the fluxes used in the composition of the body should be carefully studied. When compared with other fluxes, potash felspar is a slow and safe fluxing material because of its high viscosity during fusion. A highly viscous flux does not allow the body to get deformed by its own weight at the high temperature when the whole mass of the body is in rather a soft condition. Potash silicate is more viscous than soda silicate. Ferrous iron produces a more easily fusible flux with greater fluidity than MgO . Lime in this respect is the most dangerous flux as it produces a very low-viscous fluid which easily deforms the products if slightly overfired. The ultimate fluxing effect is governed by the eutectic mixtures formed inside the body composition due to the presence of different basic oxides and their relation to the silica content.

The amount of silica present in an earthenware body mainly governs its behaviour towards its subsequent glazing. According to our practical experience the total silica content should vary between 70-75 per cent and alkalis between 3 to 4 per cent for bodies that are fired between cones 2-5. The average alumina content for such bodies is about 24 per cent. In other words the amount of quartz or flint used in a fine earthenware composition should always exceed 30 per cent as otherwise the glaze applied on the body is expected to craze, the final effect of course is governed by the temperature and conditions of firing of both the biscuit and glost fires.

Effect of firing. In order to understand the changes that take place inside an earthenware body during firing the study of the three graphs will be very useful. In fig. 22 are given three graphs showing the loss in weight due to firing at different temperatures of a kaolin K, one coal measure fire clay F and an

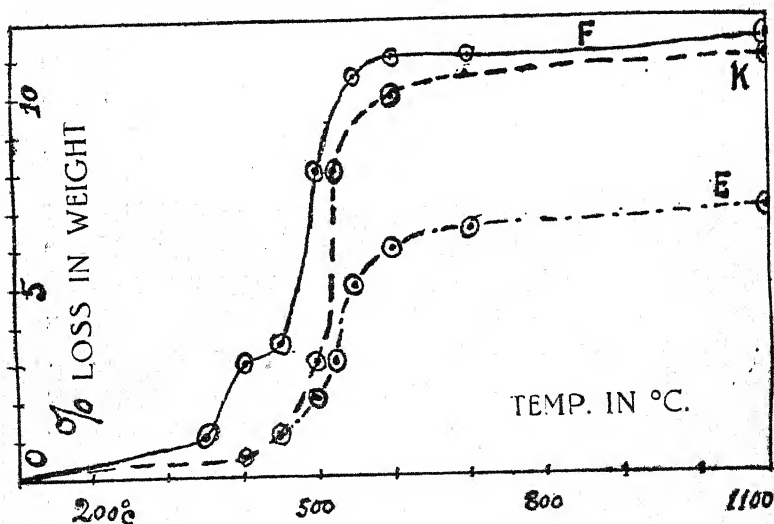


Fig. 22 Loss in weight of different substances.

ordinary earthenware body E. The trial pieces were made by pressing square tiles two inches side and allowed to dry in air for several days till bone dry. They were then weighed and fired in an electric oven with slow rise of temperature which was noted by a pyrometer.

It is interesting to note that the kaolin loses very little in weight below 460°C while the fire clay slowly loses weight upto about 350°C and then there is a sudden jump up to 400°C . These two stages are mainly due to the different natures of organic matter present in coal measure fire clays which are burnt off at different temperatures. The earthenware body loses about one per cent in weight upto 450°C but after that temperature there is a sudden jump for all the three curves. This loss in weight is mainly due to the liberation of the combined water in the clay substances and in an ordinary earthenware body the total loss amounts to 6-8 per cent of the whole mass. As the major portion of this loss in weight is due to the escape of combined water from the clay which is converted into a very large volume of steam at this temperature it is quite obvious that the rate of firing of the earthenware biscuit oven should be very slow with plenty supply of fresh air in order to carry away the large volume of steam.

In the fig 23 is shown the effect of heat on an earthenware body E in respect of the changes in volume.

The curve shows an expansion of the volume upto about 800°C . This expansion is mainly due to the inversion of quartz present in the body mixture. Above 800°C the body begins to contract but very slowly upto 1000°C but above this temperature a very rapid contraction takes place.

It is generally assumed that this contraction is mainly due to the combination of the dehydrated clay and free silica to form mullite and their solution in the glassy melt and it is evident that here is another critical period when great changes take place in the clay body, and

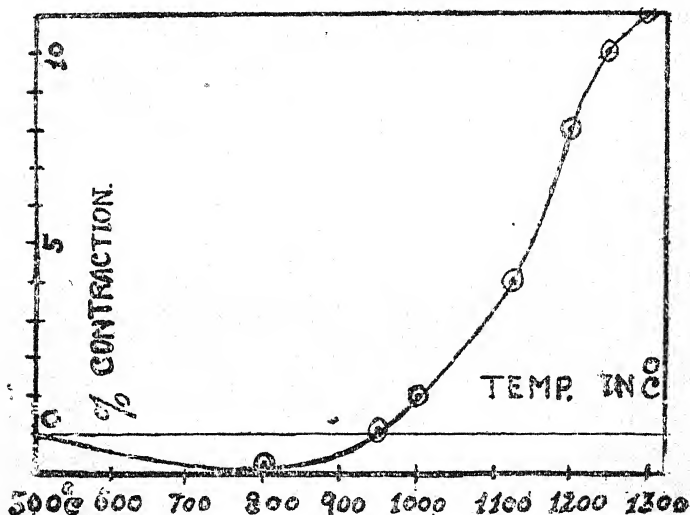


Fig. 23. Changes in volume of an earthenware body.

consequently when the firing should be slowed down. The value of soaking the oven at the finishing temperature is obvious when we consider the rapid rate of contraction of the clay body at this stage.

We can now form some idea as to the proper rate of firing an earthenware biscuit oven in order to produce the best result. During the first stage the rate of increase of the temperature should be slow until the oven is heated throughout to about 150°C when the

hygroscopic and deposited water will be driven off. Then this rate may be increased until the oven is about 450°C or the bags are just red, and from this time to about 600°C when the oven will be solid red throughout the rate should be again slow. From 600°C to 950°C the rate may be greatly increased and must then be steadied until the oven is fired up, care being taken to soak the oven at the finishing temperature for a longer or shorter time according to the size and solidity of the ware.

The following firing chart has been developed from practical firing of big earthenware ovens.

Range of temp. Hours of firing. Rate of temperature rise.

Up to 150°C	15	10°C per hr.
150 — 450°C	15	20 " "
450 — 600°C	15	10 " "
600 — 950°C	14	25 " "
950 — 1120°C	14	12 " "

Total 73 hrs.

The soaking period varies from 2-4 hrs.

The cooling of the oven up to 800°C is rather rapid, within 10 hrs afterwards the rate should be slowed down to avoid cooling cracks. Earthenware articles are always fired twice. The first firing or the biscuit firing is done between 1100°C to 1200°C and the second firing or the glost firing is done between 1000°C and 1100°C .

Biscuit Placing. All articles are placed inside saggars, and these saggars are piled up on one another

in concentric rows called "rings", inside the oven. There are 5 or 6 such rings in a normal sized oven. The central ring is made of empty hollow saggars in order to carry the flames from the central hole or the *well* at the base, to the top or the dome of the oven. A space of about 2 feet is left under the dome or crown of the oven in order to allow the hot gases to circulate and the smoke to escape through the flues built on the crown which can be opened whenever needed.

In filling the saggars for the biscuit burn, fine round grained sand, free from iron is used for embedding the articles. Plates, saucers and other similar fat articles are piled on strong flat articles, generally a previously burnt ware of similar shape and called a *setter*. The sides of the pile are covered with sand to give each article support during firing and to protect them from going out of form. Big oval dishes are carefully embedded in sand one above the other and the two ends of the top dish are weighted with lumps of sand. Cups are placed in saggars, in twins, boxed to each other. All articles placed inside the saggars are sprinkled with a thin layer of sand to protect them from the flames and dirt that may drop on them during firing.

Tiles. These are piled up one above the other on a setter about twelve in each pile, and covered with a biscuit tile to keep the pile clean. A little more than an inch of space is left on the top of each pile for the hot gases to circulate inside the saggars. Tiles

go to the oven direct from the press, so the firing is very slow during the smoking period. It takes about 130 to 140 hours to finish the biscuit firing of tiles, the temperature rising finally to about 1100°C . It takes nearly a week to cool an oven, as rapid cooling is not safe on account of cracking of the tiles during cooling,

For the firing of a biscuit oven with tiles, the following chart is fairly representative.

Temp. up to 100°C is raised in 30 Hrs.			
From 100°C to 150°C	„	„	10 „
„ 150°C to 200°C	„	„	4 „
„ 200°C to 400°C	„	„	12 „
„ 400°C to 700°C	„	„	23 „
„ 700°C to 900°C	„	„	20 „
„ 900°C to 1100°C	„	„	30 „
			<hr/>
			total 129.

A long soaking is given to avoid dunting. The cooling takes about a week.

Biscuit defects. After drawing the articles from the oven, they are sorted and the defective pieces separated. The average loss in biscuit firing in a well controlled factory varies from ten to fifteen per cent. The defects generally arising from biscuit firing may be classified as follows.

1. Wreathing, or small swelled lines on the biscuit ware. This defect originally arises during making,

caused by air being enclosed between the clay which swells up after firing. It is apparent both on cast and jolleyed wares. It can be removed by fettling and turning the ware before firing.

2. Crooked wares, are caused by defective biscuit placing and overfiring of the ovens. In the latter case the wares would begin to vitrify and lose their shape.

3. Specky wares, are caused by the iron particles present in the placing sand or firing the wares in green saggars. If the oven gas is too much smoky it may cause specks due to the reduction of iron particles.

4. Dunted or cracked wares, are caused by bad placing, rapid firing in the beginning, admission of too much cold air during firing, and too rapid cooling of the oven. Too much finely ground flint in the body mixture also helps the ware to crack in firing.

5. Browned wares, are caused by the flashing of the kiln atmosphere. The cause of this flashing action has been dealt with in Chap. VI when dealing with the salt glazing.

6. Scums, or vitrified patches on the surface of the ware, are formed from the soluble salts present in the body. This defect generally appears at the edges of the ware where the evaporation is greatest. These scums often prevent the glaze to adhere firmly with the body and the glaze scales off from those patches.

The two main defects observed from biscuit tiles are wedging and cracking or dunting.

Wedging is mainly due to defective pressing and firing. If the pressure applied in making a tile is not uniform on all sides, there will be unequal contractions during firing and one side of the tile will be shorter than the other. This defect is known as the wedging of tiles. Similarly, while firing the tiles, if the temperature on one side of the saggar is higher than the other side there will be unequal contractions in the tile which will lead to wedging. This firing defect mainly arises due to faulty placing of the saggars or bad floor design.

Tiles are often found to crack due to their too much very fine grained silica content. In order to control this defect modern tile factories always determine the surface factor of the ground silica used. The average surface factor for ground silica for this purpose varies from 235-240 with the following analysis :—

Fine 50 per cent. Medium 35 per cent. and coarse 15 per cent.

As tiles are not dried before firing, its heating up must be very slow to avoid cracking. Similarly the cooling down of the oven after firing should also be slow and uniform on all sides specially after the temperature of the oven has gone down to 800°C. If these cares are not taken we may expect heating up or cooling down dunts from tiles.

Glazes. The glazes used on earthenware biscuit bodies are of alkaline, plumbiferous, or calcarious types. They mature at various temperatures according to the

nature of requirement. These glazes are generally clear enough to show the decorations below them. High-alkali glazes are now a days seldom used as they have a great tendency to craze.

An alkaline glaze can be prepared from the formula.

0.7 alkalis.

0.3 CaO

0.15 Al_2O_3

2.5 SiO_2

The relative amounts of lime and alkalis, depend on the composition of the body to be glazed. High alkaline glazes are suitable for the siliceous bodies and the calcareous glazes have to be applied to more aluminous bodies.

The plumbiferous glazes are used either raw or fritted. The former is seldom used on domestic earthenwares. A raw majolica glaze has the formula.

$\text{PbO. } 0.15\text{Al}_2\text{O}_3 \text{ } 1.75 \text{SiO}_2.$

This glaze is clear, transparent and can be compounded from :—

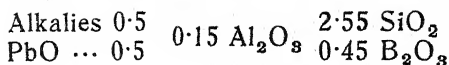
White lead, 67.3 parts. Flint, 22.6 parts. China-clay, 10.1 parts.

If the glaze is to be made opaque in appearance, the following recipe with zinc oxide may be used.

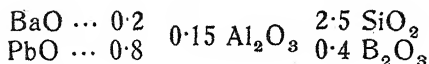
White lead, 54. China clay, 20. Flint, 16. Zinc Oxide, 8. Whiting, 2.

E. Berdull published in Sprechsaal (1915) the following fritted glazes which are stated to be non-poisonous inspite of their high lead contents.

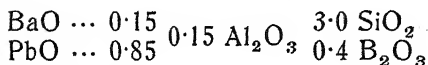
For temperature 650°-670°C



For temperature 790°-800°C.

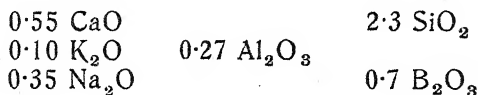


For temperature 1000°C.

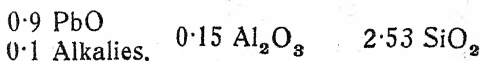


The plumbiferous glazes used on fine earthenwares are generally composed from two different frits—the borax frit and the lead frit. This ensures better non-solubility of the glaze in acids. Since the frits are glassy materials without any binding power, some china clay and white lead has to be added in the glaze mixture to give it a plasticity, without which the glaze when dry would tend to fall off from the biscuit body. The formulas for the frits and the glaze body are as follows.

Borax Frit.



Lead Frit.



Glaze Body.

0.35 PbO		2.8 SiO ₂
0.35 CaO	0.28 Al ₂ O	
0.30 Alkalies.		0.45 B ₂ O ₃

The glaze matures between 1020° to 1040°C.

For the recipes of the frits and the glaze see the chapter on calculation. Two fritted lead glazes are given below.

Frit Mixture.

Red lead.	...	67
Quartz	...	28
China clay.	...	5
		<hr/>
		100

Mill Mixture.

Frit.	...	80
China clay.	...	8
Quartz.	...	5
		<hr/>
		Temperature 980-1020°C.

Frit Mixture.

Red lead.	...	20
Borax.	...	22
Quartz.	...	30
Felspar.	...	17
Marble.	...	11
		<hr/>
		100

Mill Mixture.

Frit.	...	82
Felspar	...	10
Kaolin.	...	8
		<hr/>
		100
		<hr/>
		Temperature 1040-1060°C.

Two raw lead glazes for fine earthenware are given below. The first one maturing between temp. 1000°C-1040°C and the second one between 1100°-1120°C.

		1	2
White lead.	...	60	40
Quartz	...	25	25
Felspar.	...	7	15
China clay.	...	3	5
Zinc oxide.	...	—	5
Marble	...	5	10
		<hr/> 100	<hr/> 100

Leadless glazes are often used on white wall tiles as owing to the heavy weight of lead oxide, the amount of led glaze required is greater than that of leadless one, to cover the same surface area the ratio is often as high as three to one. These glazes are also largely used now a days, on domestic wares in order to lessen the danger of lead poisoning. Lead glazes are more glossy than leadless ones and have greater range of firing. Leadless glazes have greater tendency to devitrify than lead ones.

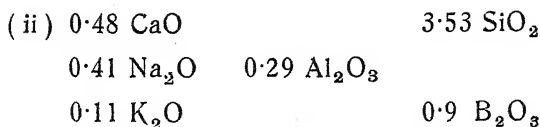
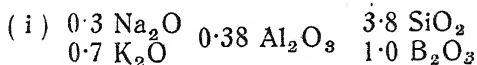
A few recipes of leadless glazes are given below.

A. Raw leadless glazes :—

Felspar.	...	40	45	50
Quartz.	...	25	20	22
Whiting.	...	10	10	18
Kaolin.	...	10	10	10
BaCO ₃	...	—	15	—
ZnO	...	15	—	—

The above glazes mature at about 1120°C . The third one is softer than the other two.

B. Fritted leadless glazes.



These glazes mature at about 1000°C . The CaO may be partly replaced by BaO with advantage. It increases the gloss and fusibility of the glaze but too much BaO increases the tendency of the glaze to craze.

Matt glaze. If the glaze is allowed to crystallise or devitrify it loses its glossy character. When properly produced, this dull glaze has a pleasing effect and known as *matt glaze*. Glazes rich in easily crystallisable oxides like CaO and ZnO and low in alumina become matt on slow cooling. Alumina increases the viscosity of the molten glaze and hinders the formation of crystals. If we take a raw majolica glaze consisting of white lead 67 parts, quartz 23 parts and china clay 10 parts and add to it 10 parts of whiting, a pleasing matt appearance will be obtained. With 10 parts of ZnO the glaze will remain glossy but with small dull patches. If the ZnO is increased to 20 parts the whole glaze will

devitrify with a dull surface. Calcined china clay produces better matt effect than raw one.

A leadless matt glaze can be obtained by fritting together :—Borax 40 parts, felspar 20 parts, quartz 25 parts and whiting 15 parts. Add in the mill, frit 70 parts, china clay 10 parts, and zinc oxide 20 parts. This glaze matures at about 1000°C and with slow cooling produces a matt surface.

A good matt glaze can be prepared from the following recipe :—Felspar 36, whiting 10, white lead 38, china clay 12 and copper oxide 4 parts. The glaze matures at 1000°C with a very pleasing matt green surface.

Enamels. When ferruginous clays are used for making the pottery wares, a stanniferous opaque glaze or enamel is often used to cover the coloured body. This glaze may be left milk white or coloured with suitable colouring materials. A white enamel suitable for red clay bodies may be made from the following formula.

0.5 PbO

0.4 Alkalies 0.2 Al_2O_3 3.4 SiO_2

0.1 CaO. 0.7 SnO

The tin oxide is best added in the mill and not in the frit mixture. A few recipes of raw lead enamels are given below.

	1	2	3	4
White lead. ...	60	58	60	65
Quartz. ...	24	20	22	25
Felspar. ...	—	7	—	5
Fire clay. ...	12	10	12	2
Red oxide. ...	—	5	1	—
Pyrolucite. ...	4	—	3	—
Cobalt oxide. ...	—	—	2	—
Chromic oxide. ...	—	—	—	3

No. 1. Is violet brown. 2. Teapot brown. 3. Black.
4. Green.

These glazes mature between 950-1000°C. The application should be thicker than normal.

After the glaze dipping the wares are first dried either in an artificial drier or on the drying racks. Then the glaze coating from the feet of the wares is brushed off so that the wares may not stick to the saggar bottom during the glaze firing. Sometimes these feet are oiled before glaze-dipping so that the oiled portions do not take the glaze.

When big articles which are too heavy to handle easily, are required to be glazed, sprayers are generally used for the purpose. In glazing wall tiles, several types of machines are in use. The one most commonly used for flat tiles, consists essentially of two rollers through which the tiles have to pass. The upper roller is thickly covered with rubber, and it presses the tiles on to the lower one which carries the glaze

and imparts a thin coating of it on the tiles passing over it.

There is another arrangement for showering the glaze from above on angular or other types of tiles which cannot be passed through the rollers.

Glost placing. The filling of saggars for the glost burn, requires some skill and care, because the glaze coating necessitates each piece of ware to be separated from the others, as otherwise, when the glaze begins to soften on firing, the pieces would get stuck to one another. Special refractory articles of different shape and size are used for this purpose which support the wares only at points or small parts. All these supports have different names according to their shapes, and the methods of using them depend entirely on the shape of the ware to be supported. Thus, *thimble* or small hollow cone shaped pieces, fitting into one another and having a small projection, are used for placing plates or other flat articles. *Cock spurs*, are little triangular pieces having three lower points on which they stand, and one upper point to support the ware. These are also used for separating flat articles such as dishes plates etc. *Saddles* are long triangular strips with sharp edges, and *headpins* are small triangular pieces used for supporting hollow and other articles.

These supports are made of common fireclay pressed into the required shape by means of small hand lever presses. It is better to coat these supports

very thinly, with a hard glaze so that their edges are sharply defined and do not break away easily.

The innerside of each glost saggars is brushed with a glaze slip, often washings from the glaze tub. This prevents the porous saggars from absorbing the glaze vapour generated by heat, from the articles placed in the saggars. Glost firing generally takes about 30 hours, temperature rising to about 1050°C .

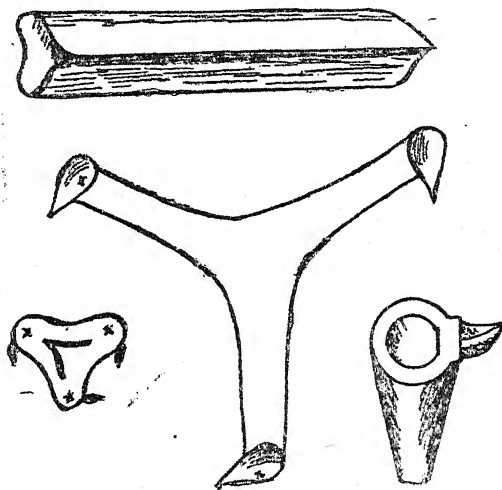


Fig. 24 Different supports for glost firing.

Decoration. Hand painting is largely practised for decorating fine earthenwares. The wares may be painted either on the biscuit state or on the glazed surface. In the former case special under glaze colours are used, while for the latter, enamel colours are necessary.

With suitable choice of patterns and colours, articles can be cheaply and artistically decorated by the combination of lithography and aerography.

Enamel Firing. It is generally done in a muffle oven. The firing lasts to about 10 to 15 hours and the temperature ranges between 700-900°C in general. The upper half of the oven is always hotter than the lower half and such articles as lithographed and aerographed wares which require harder fire are placed on the top portion of the oven. After each firing the inside of the muffle is white washed with china clay mixed with a little silicate of soda, all crevices on the joints being filled up with clay and fine grog.

CHAPTER VIII

TERRA COTTA

The term terra cotta is applied to all pottery wares made of common clays and without any glaze. The chief articles included within this group are, common bricks roofing tiles and unglazed red clay pottery.

For the production of bricks, tiles etc. which are burned only to harden and give them resistance to the influences of air and moisture the clay should be such that certain constituents of it should possess comparatively low melting points while the others are less fusible by the action of heat. The latter act as it were as the skeleton which preserves the form of the object while the former melt to surround and protect the unmelted portion. The brick clays contain true clay substance in a greater or less degree which gives to them the plasticity. They are however mixed with the debris of rocks in greater or less quantity and these nonplastic substances have always an essential influence on the properties of the whole clay. The residues of felspar and augite which are often found in clays are as a rule the most fusible constituents ; then comes the clay proper, which sometimes is so fusible that it may serve as a flux, and again often very refractory, when it helps to retain the shape ; quartz and other debris of rocks, assist in maintaining the skeleton of the ware but there is no definite

data regarding the proportion in which the fusible and the refractory constituents must stand to each other to give the best result.

Another important point regarding the clay is that the articles must show as little shrinkage as possible, both in drying and burning. The difficulties which are caused by the drying shrinkage may be overcome by working the clay as stiff as possible, or the crooked bricks or tiles may be straightened by re-pressing but to control the burning shrinkage, is difficult. If the shrinkage in burning is great, the ware may go out of shape. The difficulties of retaining the exact shape of the articles are the less, the fewer pores the clay contains after drying.

Colour on burning. The number of substances which colour clay is quite limited if we neglect the rare elements such as vanadic acid or titanitic acids which are present in common clays in very small quantities. Practically speaking, the colouring elements and substances which influence the production of colours in clays can be resolved to iron and manganese oxides and the carbonates of lime and magnesia. The colouring property of these oxides depend on their physical condition and chemical composition, as well on the texture of the clay after burning. Manganese oxide usually exists in such a small quantity in common clay that it has very little independent action in producing any appreciable colour, except helping and modifying the tone of the colour produced by iron oxide. Lime, magnesia, and alumina, have no

colouring power by themselves, but their presence greatly modify the colour produced by iron.

If the content of iron oxide in a clay is small and that of alumina large, and the burning temperature is high then the clay will assume only a more or less yellow or yellowish brown colour, which with a smaller content of alumina and larger amount of iron passes regularly through all shades from yellowish brown to reddish brown. Only with a content of about 5 per cent of iron oxide does a decided red colour appear, which is intensified still more by higher content of iron. Lime and magnesia have also a powerful bleaching action on the iron colour. If the content of lime is about double that of iron oxide the red colour of the iron oxide disappears completely at a sufficiently high temperature, the colour being converted into a yellowish green shade.

The influence of the atmosphere present inside the kiln during burning is also well marked. The action of reducing atmosphere is to change the compounds of ferric iron into ferrous ones or even to metallic iron, and the clay assumes a grey colour or even black in presence of much iron. On being exposed to an oxidising atmosphere, the ferrous iron will change into a yellow or red oxide. In periodic kilns reduction occurs, as a rule, in the first period of the burn, becoming weaker towards the end. In continuous kilns however the condition will always be oxidising in all kilns unless reduction is provided for. Cooling will take place in the oxidising atmosphere.

The sulphur present in fire gases, derived from the fuel, plays an important part on the colouring property of a clay. This is specially prominent in the case of calcarious clays on whose surface a formation of calcium sulphate takes place. If the lime thus separated can not enter into the formation of the silicate, the colouring effect of the iron oxide will not be influenced by the lime and sometimes a very intense red colour will be produced even in a highly calcarious clay in the places exposed to the oxidising fire. On reduction these red patches will disappear but owing to the absorption of sulphuric acid, the colour of the places which once have become spotted will differ in shade.

The temperature of burning also modifies the colour of the clay to a great extent. Iron oxide assumes a darker shade with a continually rising temperature and this is also true for its compounds, so that clays which are burned at a higher temperature possess in general a dark colour. But when the clay contains some amount of lime the increase of temperature would cause decrease in the colour due to the iron oxide. Only in clays free from lime the properties of the iron oxide alone are the governing factors.

Mc vey (1936) is of opinion that the colour in fired clay is due to sinterising that is the expansion of grain size due to heat; which results in a closeness of particles. In an experiment he has shown that iron oxide may be wholly oxidised and yet be black, due to sintering. Sheldon (1935) contents that devitrification

or crystallisation and the solution of the crystals strongly influence the colour. When the red crystals developed get dissolved, specially into the glassy melt, the colour of the products suffers. The factors contributing to solution of these crystals are, high temperature, reducing atmosphere, and the presence of dolomitic glass.

Bricks. As a convenient building material, bricks made of burnt clay are used from time immemorial. The Egyptians are said to have used bricks as early as twenty thousand years ago and in India bricks were used for building dwelling houses about four thousand years before Christ.

The dimensions of building bricks were and still are quite different in different countries. The bricks used by Egyptians and Romans were much larger than those made at the present time, but bricks used in India in olden days were noticeably smaller in size. The present tendency in all countries is to make the bricks of sizes near about $9" \times 4\frac{1}{2}" \times 3"$, while the standard size for English bricks is $9 \times 4\frac{3}{8} \times 2\frac{5}{8}$ inches. The width of the brick should be such that the brick layer may easily take the brick between his fingers when it is lying flat and the length should be nearly double the width for convenience in building. The thickness of the brick should not be more than three inches for thicker bricks take too long time for drying and cause other troubles.

Moulding. The oldest method of making bricks is by hand moulding and this is still largely practised

in India and other countries where small brick yards spring up to supply only the local requirements using clays which require but little preparation. The moulding is always done in wooden moulds well sanded, the lump of clay also being rolled in sand. The moulder cuts off the required amount of clay from the pile, rolls it in sand and throws it into the mould cutting off the excess clay with a wire stretched across a curved piece of wood, like a bow. After the drying, the bricks are set in clamps with alternating layers of coal which are set on fire through flues left open for this purpose. The admission of air during the burning which according to the size of the clamps, lasts from two to six weeks, is regulated by piercing the coating of clay around the walls of the clamps in places according to the judgment of the burner.

This method is, without doubt, best adopted for temporary production and if the burn is successful, owing to favourable weather, it is also the cheapest. As a rule with a normal clamp burn, one eighth of the bricks are waste, owing to melting and breaking; but a loss of one quarter is not uncommon in unfavourable weather.

Special *face bricks* are now-a-days largely used for the outer portions of buildings exposed to the atmosphere. These bricks have a dense surface which are less easily attacked and destroyed by atmospheric agents than common porous bricks. The colour of the exposed surface is also very important. It should be uniform and pleasing. Uniformity of the clay used and

care during firing are essential factors to produce good face bricks. Sometimes a thin coat or wash is applied on the face bricks before burning in order to make the surface hard, durable and pleasing in appearance. The coating vitrifies at about the same temperature necessary for burning the bricks.

Addition of varying amounts of caustic soda in the brick clay has been found to be very useful in hardening the brick at lower temperature of firing. With this addition varying from 1.5 to 7 per cent according to the nature of the clay the products fired at low temperature of about 500°C show properties similar to products fired at high temperature.

For firing common bricks various types of kilns are used, the modern tendency being towards tunnel kiln. The advantages of a tunnel kiln are, in the economy of fuel, labour and breakage, and an improvement in quality.

Blue bricks or paving bricks are made from clay containing high percentage of iron oxide. The burning is carried on in the usual way at the beginning but towards the end of the firing and before the pores on the surface of the goods begin to close up, the fire-mouths are heavily loaded with coal and the air passages closed as far as practicable in order to produce an intensely reducing atmosphere inside the oven. As a result of this treatment, the iron oxides are reduced and combining with silica form black or bluish-black colouration on the surface of the ware. If the pores are closed before the reducing action is

started, the cores of the ware will remain red or brown with bluish patches on the surface which will not be lasting. The cooling of the oven should be carried on under the same reducing condition otherwise some iron on the surface will reoxidise leaving reddish patches on the surface which will spoil the colouring effect. The reducing condition of firing helps the brick to vitrify better and become stronger.

Sand-lime Bricks. In sandy districts where clay is not abundant sand-lime bricks offer great possibilities. They also afford a useful means of converting into a commercially profitable product, the waste clinkers lime and slags from large corporations and firms. The so-called sand-lime bricks are made by mixing sand with slaked lime and subjecting the mixture to the action of steam under a high pressure. The reactions that take place within the composition are supposed to be :—

The recarbonation of lime on exposure to the atmospheric actions. The precipitated carbonate of lime thus formed is gelatinous in nature and has a good binding power when wet but sets hard when dried up.

Partial combination between lime with silica and alumina to form a silicate or aluminosilicate of lime called hydraulic lime, under the action of steam and pressure. This hydraulic lime sets hard like cement, binding other aggregates into a hard mass.

The term sand is used here for any highly siliceous material such as slag, clinkers, grog etc. in a powder form. The fineness of the material should be such

that at least ten per cent of the powder should pass a lawn no. 150 and the rest through lawn no. 20. Too much fine grains whilst increasing the tensile strength of the bricks, diminishes the compressive strength considerably. The amount of clay in the sand should be less than five per cent. Although one or two per cent of clay is desirable. When pure siliceous sand is available, it gives the best result.

The lime should be as pure as possible. The proportion of lime required is from 10 to 15 per cent of the weight of sand, but the actual amount which gives the best result with the particular sand must be determined by experiments and followed rigidly with the same materials.

The mixing is done in two ways, in the first process the lime is thoroughly slaked with water before mixing with the sand. It is essential that no unslaked lime should be present in the mixture as this would make the bricks unsound and weak. In the second process the dry sand is mixed with the unslaked lime in a mixing machine. Water is then added to slake the lime and make a plastic mixture. The mixture is stored for two or three days in order that the water may be uniformly distributed in the mass and the lime completely slaked.

The mixture is then moulded into bricks in machines under a heavy pressure of 1 to 2 tons per square inch. It is claimed that bricks made from the plastic mixture increases the strength of the articles. After moulding the bricks are placed on wagons and hardened in an

auto-clave where they are subjected, for about 8 to 10 hours, to steam at about 180°C and a pressure of 120 lbs. per square inch. On removal from the boiler the bricks are ready for use but still fragile. Their strength is increased and quality improved by storing them in open sheds for several weeks or months. Sand-lime bricks when properly made, serve the same purposes as clay bricks but the difficult process of burying clay bricks is entirely avoided in this case. The average crushing strength of sand-lime bricks is about 2, 500 lbs. per square inch. Another advantage of these bricks is that they have less tendency to scum or efflorescence than ordinary clay bricks and this is a great boon for countries with damp climate like Bengal and Assam in India.

Tiles. The use of tiles for covering the roofs of dwelling houses dates from very ancient times. What is known as Roman tiles in the western countries, were used in modified form in India long before Romans learnt the use of tiles. In fact the Romans imitated the Greeks in this kind of covering for the roofs of their houses, and the Greeks, it is believed carried the art from the East.

Flat or plain tiles, are largely used in Great Britain. They are ten to fifteen inches long and five to ten inches wide with one or two hooks at one end to prevent them from sliding down on a sloping roof.

Marselles tiles, have grooves and ridges to attach them to each other and are extensively used in France and other countries of Europe as these tiles cover

more space than other tiles of non-interlocking type. In India interlocking tiles of similar type are made in large quantities specially for roofs of better kinds of houses. This industry at present is mainly concentrated towards the southern parts, but there is enough scope for extending the industry to many other parts of this country.

Tile works are generally constructed on sites where there is an abundance of suitable clays. It is well known that in every excavation where clay is obtained, there are several differing seams or strata. Hence it is of great importance that clays from these different seams should be so blended as to give a satisfactory body. The knowledge of blending the various clays available is the first essential in this branch of the clay industry and any effort spent in this direction will never be in vain. If clays are allowed to mature or sour for some days, specially after the pugging process, better results are obtained than using the clays direct from the pits. The clay for this purpose should be rather sandy as highly plastic clays increase both dry and firing shrinkages which cause warping both in drying and firing. The sand particles in the clay should be of fine grains otherwise the porosity of the fired tiles will be high which is not desirable.

There are generally two methods for making these tiles. The plastic and the semi-dry method. The consistencies of clay mass for these two methods are the same as used for making common bricks by similar processes. With the plastic mass the tiles can be hand

pressed in wooden or metallic moulds sometime lined with plaster of Paris or they can be made by a machine with similar principle as used for making wire-cut bricks. Clay used for plastic moulding should not be very soft. A soft clay shrinks more and increases the porosity of the body more than a stiff clay. Moulds used for semi-dry body are made of polished cast iron as great pressure is required in this process. The moulds are oiled to prevent the body from sticking to them. Tiles made by this method are not so satisfactory, as much of the troubles caused by lamination and decay have been largely in connection with tiles made by very high pressure from dust body.

In India, tiles largely used for common dwelling houses are of Roman type with slight modifications. They are invariably made by the plastic process. The flat slabs are made by hand pressing on wooden moulds dusted with sand, while the round covering tiles are made on potter's wheels or *Chaak*. A hollow cylinder of the size of the round tiles is first made on the wheel which is then cut into halves with a piece of wire. These round tiles as well as the flat ones, are made slightly tapering at one side, so that they can fit to one another and make the roof watertight. These tiles are not very strong as they are made light to avoid overloading the roofs and also they are often fired at low temperature.

Burning. Tiles are best fired in down draught periodic ovens unless continuous ovens are made specially suitable for them. Horizontal kilns of the

Newcastle type are largely used for firing both tiles and bricks. The manner in which tiles are placed in the oven largely depends on their shape. Tiles are generally set on their edges close to each other but leaving sufficient space for the hot gases to circulate. Tiles are set in ovens in a slightly moist condition for if they were perfectly dry much loss would occur owing to breakage, as it is impossible to set the tiles satisfactorily unless there is some plastic strength in them due to the moisture present in the body. In burning tiles much consideration should be made on the colour of the finished products for which absolute control of the atmosphere inside the kiln is necessary. The heating up and the cooling periods of ovens burning tiles should be very slow in order to avoid unnecessary loss due to dunting of the ware.

The colour of the tile is rather an important factor for its manufacture. The general tendency is to produce red tiles but black tiles are also used in many countries. To produce uniformly red tiles with a smooth surface a wash consisting of red ocher and soda silicate may be applied on the tiles before firing. This is specially helpful if the clay contains low iron oxide and high percentage of lime, and not very homogeneous. The wash forms a very thin skin of uniform red colour and lowers the soaking power of the tile. This skin also prevents the formation of algae or moss for a long time. Black tiles are made in the same way as blue bricks from highly ferruginous clays.

Common Pottery. These wares are very cheap, light and porous, and are generally made from common fusible clays having great plasticity. The *Kumbhakars* or potters in India use the alluvial clays or silt deposits from rivers and ponds, and these clays are remarkable for their plasticity and homogeneous composition. The articles made from these clays are very porous and are used in India mostly for cooking and storing water for drinking.

The preparation of the clay for this kind of pottery is very simple. The clay is only kneaded with water mostly by treading under feet and kept aside for some days for maturing. In most cases, specially with the alluvial deposits, the clay is used directly by the potters without maturing.

The shaping of the articles is still done in this country on the primitive type of potters wheels. This wheel, which is generally a disc of stone, is made to rotate by the man on a pivot, and fresh impetus has to be given every five minutes or so, to keep it rotating. Half the time of the potter is thus taken away to rotate the wheel only. If improved potting wheels as described in chapter II are used the production of wares can be increased to a great extent. The self driven wheel can be employed for making articles of light nature and small dimensions but for heavier articles, a more powerful wheel driven by a boy assistant is recommended. With this arrangement both the hands of the potter are always free and he can also regulate

the speed of the wheel according to his own requirements.

Firing of common pottery in this country needs special attention, as much improvements can be done on this line. The country potters still fire their ware in open clamps where there is scarcely any control over the process of firing and the temperature can not be raised sufficiently high if necessary. The loss is also very considerable due to breakage and bad firing which is entirely dependent on the weather condition. The heat loss due to insufficient combustion of fuel and radiation can not be controlled in open clamp firing. A properly constructed potters oven can much improve the present system and produce wares of superior quality reducing the loss due to firing.

As wood is the most easily available fuel in the villages of this country, a small wood fired kiln would be most useful for our country potters. The sketch shown in fig. 25 is of a very simple type of up draught kiln which can be constructed easily with red bricks at a very small cost.

The top of a small kiln can be closed temporarily with clay slabs after filling the chamber with the articles to be fired. The firing is done from below with wood. The long flames of the wood fire pass through the holes in the floor of the kiln, heat up the wares kept inside the chamber and the gases then pass out through the joints between the slabs which close the top. As wood fire produces less smoke than coal,

this type of kilns specially for unglazed common pottery do not require any saggar. Hence the cost of firing

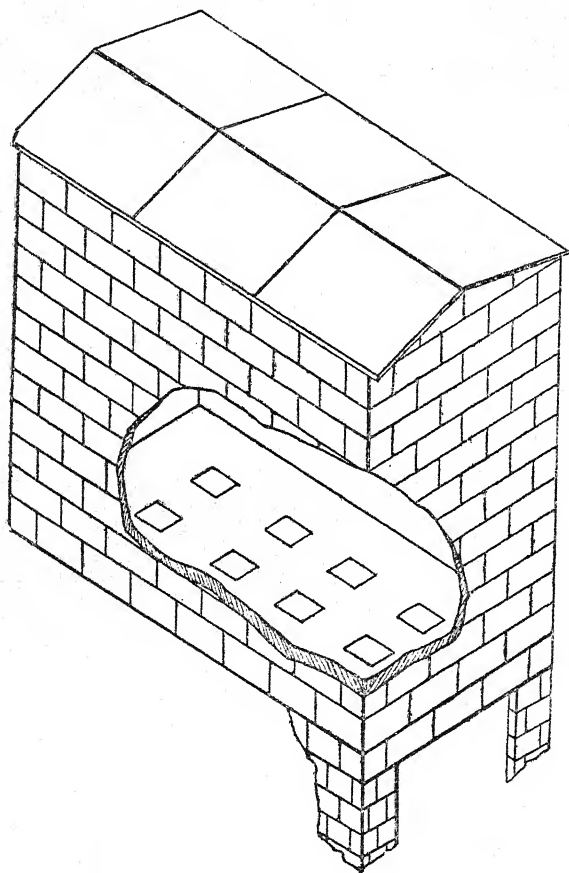


Fig. 25 A simple potters kiln.

is also very low. When the firing is finished and the kiln is allowed to cool slowly the slabs from the top are removed and the wares taken out from the top. The temperature of firing this type of ware does not go above 900°C in most cases. This simple type of kiln is used in Chunar for the glaze firing of the popular chunar pottery.

CHAPTER IX.

REFRACTORIES.

Refractory Materials. The term refractoriness is used to indicate the resistance of a material to the action of heat under particular conditions of use, but generally speaking no material is regarded as refractory which shows any external sign of fusion below "Porcelain heat" *i. e.* 1350°C — 1400°C .

The conditions of use in general are :—

- (a) Reaction of gases inside the furnace. Graphite and carborundum burn away under oxidising atmosphere while chromite or haematite get reduced in the absence of free air and lose their refractory property.
- (b) Condition of pressure while in use. A highly siliceous fire clay will stand high temperature under load better than kaolin which contains more of alumina. The squaring temperature of china clay, according to Dr. Mellor, is lowered approximately by one cone for every increase of 5.25 lbs. of pressure per square inch.
- (c) Chemical reaction inside the furnace. Magnesia or dolomite bricks will be easily attacked by molten glass in a tank furnace whereas a

silica brick will not stand in a cement or lime furnace.

According to the nature of their chemical reactions refractory materials are divided into three main groups :—

Acid Materials. Siliceous rocks Fire clays, Kaolin, Sillimanite and Kyanite etc.

Basic Materials. Magnesite, Dolomite, Zirconia, Bauxite, Haematite, Basic Slag.

Neutral Materials. Chromite, Graphite, Carborundum.

The siliceous materials generally used for making refractories are, siliceous rocks such as quartz, quartzite, ganister etc. and white sand. The siliceous rocks differ widely in composition but for refractory purpose they must contain at least 90 per cent SiO_2 , the main impurities being alumina, iron and alkalies which should not exceed 5 per cent except the alumina.

Crystalline quartz is found in abundance throughout India but generally not used for making refractories. *Quartzite* is a rock consisting of an irregular matrix of quartz crystals imbedded in a cement of silicic acid. The Small crystals of quartz in quartzite are usually coloured yellow to brown owing to impurities. Quartzites are non porous and have a smooth fracture.

Ganisters are compact sedimentary siliceous rocks of very fine granular texture. They often contain up to 10 per cent of clay and are slightly plastic when ground

in water. Unlike Quartz or quartzite they do not require any binding material to form them into bricks.

Typical Analyses.

	<i>Soft Ganister.</i>	<i>Quartzite.</i>
SiO ₂	88.4	97.85
Al ₂ O ₃	6.4	1.81
Fe ₂ O ₃	1.7	0.38
CaO	0.7	—
MgO	0.4	—
Alkalies	—	—
Loss	2.4	0.32

White sand for refractory purpose should contain more than 95 per cent of SiO₂ and less than 0.5 per cent of iron, lime or alkali each. The grain size should be as uniform as possible generally passing through 20-25 sieve.

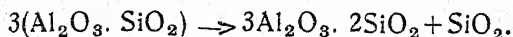
Occurrence. Borgarh in Allahabad District, Jubbulpore, Bikaner state, Pandanlu and Sankeda in Baroda state and Jaijon in the Punjab.

Sillimanite (Al₂O₃. SiO₂). Natural sillimanite occurs as long needle shaped crystalline and fibrous aggregate. It has very high temperature (1850°C.) of fusion. It is generally coloured brown or grey and is very hard to grind. The ground material is often contaminated with iron from the grinding mills which has to be separated by electro-magnet. The powder is devoid of any plasticity and has to be mixed with clay for

moulding. Slight contamination of iron reduces the refactoriness of sillimanite to a great extent.

Occurrence. Khasi plateau, Sare pahar, and Nongstan state in Assam, Pipra in Rewa state, Bhandara in C. P.

Kyanite. ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$). Although both sillimanite and kyanite have the same chemical formula, they differ in their physical properties. When heated to a sufficient high temperature both change into mullite— $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Kyanite is transformed at the lowest temperature with considerable increase in volume while sillimanite requires very high temperature for the transformation with very little alteration in volume.



Occurrence. Over 90 per cent of Indian output of this mineral comes from the Singhbhum district of Behar. Other minor deposits are located in Ajmer-Merwara, Rajputana, and Mysore.

The chemical analysis of a Singhbhum Kyanite shows the following results :—

SiO_2 . Al_2O_3 . Fe_2O_3 . TiO_2 . CaO . MgO . Alkalise. Loss.
38.50. 57.55. 1.01. 0.40. Traces. 0.60. 1.80.

The fire tests of this material shows the following results.

	1000°C	1100°C	1200°C	1300°C	1400°C
Volume change		1.6(-)	3.8(-)	20.0+	22.4+
True density(3.38)	3.26	3.25	3.27	2.89	2.87

P. C. E.—Above Cone 35.

It will be evident from the above data that the material shrinks up to 1200°C but above that temperature it begins to expand suddenly with decrease in the density which indicates the conversion of the Kyanite into mullite.

Magnesia. MgO obtained from calcining the natural ore magnesite— MgCO_3 , was first used as a refractory lining in 1868 but its extensive use began only after the introduction of the basic process of steel manufacture by Thomas and Gilchrist in 1880.

Pure MgO fuses at about 2800°C but commercial ones fuse at much lower temperature due to their containing impurities like iron, clay, silica etc. Pure MgO cannot be used for making bricks as it does not form into a hard mass and 6-8 per cent of impurities is always preferred for the purpose.

Magnesite chiefly occurs as greyish fine grained mass containing about 85-90 per cent MgCO_3 . The main impurities are lime, iron, clay, and silica, and on burning the mass is blackened due to reduced iron oxide.

When magnesite is calcined at $800\text{--}900^{\circ}\text{C}$ it loses about half its weight and is converted into caustic magnesia which slake and sinter with water. When the caustic magnesia is heated further it becomes denser and is converted into a crystalline hard mass known as dead burnt magnesia or *Periclase*. This change takes place with much shrinkage and increase of Sp.gr. (Magnesite sp.gr. 3.02 Periclase sp.gr. 3.6-3.65).

The temperature of calcination for making dead burnt MgO varies from 1400°C-1600°C the lower temperature being for impure magnesite. The final product should have no further shrinkage on firing. Dead burnt magnesia has got no plasticity when powdered and mixed with water but addition of 8-10 per cent caustic magnesia produces sufficient plasticity to enable the mass to form into bricks. The burnt material is often purified from lime by washing with water in perforated rotary cylinder. The final grinding is done in Ball mills.

Occurrence in India :—

- (1) The chalk hills near Salem in Madras, contains 96-97 per cent MgCO_3 , used for making bricks and export of dead-burnt magnesia. About 90 per cent of Indian output is from this place.
- (2) Seringala in Coorg state.
- (3) Trichinapoly district in Madras.
- (4) Hassan and Mysore districts in the Mysore state.
- (5) Karnal district in Madras.

Analyses of Magnesite.

			<i>Mysore.</i>	<i>Salem.</i>	<i>Salsburg.</i>
Lime	0.4	0.3	2.0
MgO	47.1	46.3	40.9
Iron Ox.	0.1	0.2	5.9
Alumina	0.1	0.3	1.1
Silica	—	0.2	2.2
CO_2	52.9	51.9	45.0

Dolomite. The name dolomite is generally used for all magnesia lime stones but truly it is a definite mineral which on chemical analysis show about 21-22 per cent MgO ; 30-31 per cent CaO and nearly 47-48 per cent CO_2 . Its chemical composition can be represented by the formula— $MgCO_3 \cdot CaCO_3$. Dolomite can be distinguished from lime stone by its—(1) Greater hardness and higher sp. gr. (Dolomite 2·8-2·9 while Calcite 2·72) and (2) Feeble attack by HCl cold.

Dolomite is used as furnace lining for the same purpose as magnesite but the latter is much better and more durable. Hence dolomite though cheaper is being replaced by magnesite for furnace lining.

Dolomite must be burned at an intense heat like magnesite so that it is thoroughly shrunk.

In order to avoid the slaking of dolomite, an addition of 10 per cent $CaCl_2$ before calcination has proved very helpful, as a binding agent for dolomite bricks. H. G. Schurcht has advised the use of iron oxide. Kaolin up to 10 per cent is used by some people but SiO_2 is useless as it forms fusible flux with lime.

Uses :—(1) In basic open hearth steel furnaces and in Bessemers converters.

(2) In lead furnaces where the slag is of highly basic character.

(3) In copper smelting furnaces.

(4) For crucible for melting basic alloys.

Occurrences. Near Jainti in Assam. Gangpur state. The deposit of dolomite at Jainti in Bengal is

perhaps the best in India. The remarkable features of this deposit are the high magnesium carbonate and low silica and iron contents.

Calcium Carbonate	...	52.00
Magnesium Carbonate...		46.70
Oxide of iron	...	0.39
Silica	...	0.20
Alumina	...	0.57
Alkalies	...	0.14
		<hr/> 100.00

Zirconia, ZrO_2 . *Zircon*, ZrSiO_4 . These two minerals are chiefly found in Brazil, Ceylone and Travancore. The former has to be purified before it can be used as a refractory material whereas the latter can be used directly after separating the iron particles only.

For purification, the Zirconia is first digested with HCl or H_2SO_4 to remove the Fe and Ti. Then it is fused with soda and borax, lixiviated with water and filtered. The solution is then concentrated and allowed to crystallise as sodium zirconate which when treated with ammonia and calcined form pure Zirconium oxide ZrO_2 .

For use as a refractory material the pure oxide is calcined at about 1400°C . to remove all shrinkage. Zircon does not shrink on heating and it does not require any chemical purification. The iron impurities are separated by electro-magnetic separators.

These minerals have got very high fusion points (2550°C), low thermal conductivity and very low coef. of linear expansion (0.00000084) and chiefly used for making sparking plugs, high tension insulators and special chemical and laboratory testing furnaces.

Bauxite. This mineral may be regarded as an impure aluminium hydroxide, the chief impurities being SiO_2 and Fe_2O_3 . The chemical composition varies very widely but for better specimens the limiting values may be taken as follows :—

Alumina	50	to 90	Per cent
Silica	3	to 25	" "
Iron Oxide	0.5	to 12	" "
Water	10	to 30	" "

Pure bauxite is softer than gypsum and has a sp. gr. of about 2.9 but impurer ones are much harder.

Commercially bauxite is divided into three groups according to their colour due to various impurities.

White bauxite. These are often coloured light grey or slight yellow. This variety is mostly used for refractory purpose as it contains the lowest amount of iron. The chief impurity in this type is silica. *Red Bauxite* has a brick-red colour mainly due to the presence of ferric oxide. It is seldom used as a refractory material. The colour of *blue bauxite* is mainly due to the presence of colloidal ferrous sulphide. Presence of more than 10 per cent of iron is objectionable for its use as a refractory material.

Bauxite is purified from the siliceous impurities by washing the powdered material in a revolving drum through which a stream of water is allowed to pass. The impurities being lighter than the alumina particles are removed by the water current.

Ground bauxite has no plasticity and it can not be used as such for making bricks. It can be used as grog in fire clay bricks, increasing the temperature resistance of the fire clay to a great extent. When used for making bricks bauxite is first mixed with 20-25 per cent clay, tempered with water, formed into rough bricks and burned at about 1200°C . to take away all shrinkage from the material. It is then ground up with more fire clay and given the final shape of the articles to be made.

If only pure bauxite is to be used it can be tempered with lime water and given the proper shape, but it is generally used for increasing the refractoriness of fire clays.

Bauxite refractories are particularly useful for furnaces where high temperature and great mechanical strength are required—rotary furnaces and puddling furnace.

Occurrence.

Bombay—Belgaun, Kohlapur state.

Kashmir—Chakar village near Jammu.

Central Province—Between Jubbulpore and Katni;
Balaghat district.

Madras—Vizagapattam district.

Behar—Mohwadand village in Palamau district, west of Lohardaga in Ranchi district.

Orissa—Ganjam district, Kalahandi state.

Iron Ores. Haematite (Fe_2O_3) and magnetite (Fe_3O_4) are sometimes used for making refractory bricks. Ferric oxide is fairly resistant to siliceous slags in oxidising atmosphere so that these iron ore bricks can be used in the flues of boilers and such other places, where the flue gases contain an excess air. These ores are sometime used as protective linings in iron furnaces where a portion of the ore is reduced and recovered in the process.

Occurrences.

Singhbhum district of Behar.

Maurbhanj state of Orissa.

Raipur & Chanda in Central Provinces.

Bhadravati in Mysore.

Basic slag. The slag obtained from the steel furnaces working Thomas and Gilchrist process is called Thomas slag or Basic slag. This is often used as a binding agent for dolomite bricks. It contains a high proportion of lime and silica hence can not be used as a refractory material alone. It is often used for making cement.

Limiting composition of Thomas slag.

SiO_2	30 to 36	per cent
Al_2O_3 & Fe_2O_3	12 to 17	„ „
CaO	48 to 50	„ „
MgO	0 to .3	„ „

Graphite. It is a peculiar form of carbon found as a mineral of greyish black colour. It is also known as plumbago or black lead. Graphite occurs in nature in two forms the flaky graphite and powdery graphite. The latter form of graphite was thought to be an amorphous form of carbon but under strong microscope this graphite reveals distinct crystalline structure. The best flaky graphite for making refractory crucible is obtained from Ceylone. If the graphite is too much flaky it will cause 'lamination trouble' and portions of the articles may chip off in flakes. The Ceylone graphite has angular grains so that the bodies made of it do not chip off like those made with other flaky graphites. The powdery graphite is chiefly used in foundry work and for black lead pencil. Artificial graphites are sometimes made from coke and tar by heating in electric furnace. It is also obtained as a by product of carborundum industry.

Graphite used for good refractory wares should contain about 90 per cent carbon and as much free from mica, iron compounds and other impurities as possible. The impurities of graphite are generally separated by grinding in a burr mill or by floatation.

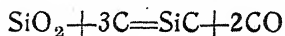
Natural graphites have sp.gr. varying between 2.01 to 2.58. It has a very low coefficient of expansion and high heat conductivity. Hence it is very insensitive to sudden temperature changes. A small proportion of graphite mixed with fire clay renders the latter less sensitive to temperature changes and increases its heat conductivity to a great extent. In this respect graphite

is much superior to other carbonaceous matters as it burns but very slowly in air. Graphite is completely devoid of any plasticity, hence some binding clay has to be used for making crucibles etc. Pure graphite has got no action on clay but its impurities may serve as fluxing agents on refractory clays.

Graphite chiefly occur in India at the following places.

Vizagapattam, Godavari Dist, Coorg, Travancore, Ajmer Merwara, Kalahandi and Patna states, Orissa and many other places throughout India.

Carborundum. Carborundum or silicon carbide SiC is an important refractory material used in special crucibles and muffles, but too costly to be used for general refractory purposes. It is prepared from sand and coke under strong electric current.



55 parts of sand and 35 parts of coke are mixed with 10 parts of saw dust and about 2 to 4 parts of common salt and charged in a special electric furnace.

The reaction takes place at about 1800°C when partial fusion begins. The charge is then cooled slowly to promote crystallisation. The saw dust is used to keep the charge porous so that CO may escape easily. The salt is added to remove the iron as volatile chloride.

The fused mass contains graphitic cores surrounded by crystalline carborundum mixed with powder carborundum and other siliceous impurities. Crude carborundum is then freed from these materials by washing and treatment with H_2SO_4 . Crystals of SiC are very hard and show varying colour from full yellow to grey or blue black. The sp. gr. varies from 3.17 to 3.2 and melting point above $2500^{\circ}C$, the exact temperature not being properly determined. It is entirely devoid of plasticity.

Commercial silicon carbides are sold under various trade names e. g. Crystolone, Silfrax, Carbofrax etc.

Chromite. It is a double oxide of chromium and iron and generally known as chrome-iron ore. A good chromite contains 68-70 per cent Cr_2O_3 which is not very common. For refractory purpose the ore generally contains 35-40 per cent Cr_2O_3 and less than 6 per cent of SiO_2 .

Chromite has a sp.gr. of about 4.5 and it melts at above $2000^{\circ}C$. The greatest shrinkage of chromite found to be near about $500^{\circ}C$. due probably to polymerisation. It can be mixed with 10-15 per cent of kaolin without losing much of its refractoriness. It is scarcely attacked by slags and for this reason it is largely used for patching open hearth furnaces.

Occurance. It occurs in Mysore and in the Singhbhum district of Behar. Very pure deposits of chromite is also found in Beluchistan.

<i>Analysis.</i>	<i>Mysore.</i>	<i>Beluchisthan.</i>	<i>Singhbhum.</i>
Cr_2O_3	51.0	56.0	51.02
Fe_2O_3	22.5	13.0	19.48
Al_2O_3	7.5	11.0
SiO_2	4.5	1.0	2.9
CaO	0.5	1.0
MgO	12.5	15.0
	98.5	97.0	

Grog. It has been found in practice that the use of certain amount of *grog* with fire clays improves the quality of the refractories to a great extent. Groggs are usually made from clean broken fire bricks or saggars by grinding them into coarse powder. The powdered grog is then separated into three grades coarse, medium and fine. The coarse particles have an average diameter of 7 m.m., the medium ones of 3 m.m., and the fine dust particles are below 3 m.m. in diameter. There is a wide variation in the proportions of these sizes used, but as a general rule, the grog must be so proportioned that the smaller sizes fill the voids between the larger particles, giving the best density and strength. In many factories, specially in England, no particular attention is paid to the grading of the grogs. The broken saggars are ground together with the fire clays in a pan roller mill and the whole mass treated with water for making new saggars etc.

The influence of grog on the refractories made with them may be summarised as follows :—

A. Effects of amount of grog.

(1) Both the dry and the fired shrinkages of the body are decreased considerably. The amount of water required to make a plastic mass is less than that required by the clays alone.

(2) Both the tensile and the compressive strengths of the mixture are decreased. In order to obtain the highest modulus of rupture the grog must not be too large so that it forms cracks or planes of weakness due to lack of the clay to bind such large particles together perfectly well. The size of the grog should be so chosen that the smaller particles fill up the voids between the larger ones giving the maximum density and strength.

(3) The apparent porosity of the mass is increased. The treatment of the grog during mixing also influences the nature and the porosity of the final body. If the grog is made from open burning clays it becomes more porous. If the grog is soaked in water before mixing with fire clay, the fine particles of the latter cannot enter into the pores of the grog and the final product after firing becomes more porous than when the grog is not treated with water before mixing with fire clay.

B. Effect of size of grog.

(1) There is no regular effect on the contraction by different grain sizes of grog ; but at high temperature very fine grogs show greater shrinkage due to incipient fusion of the particles.

(2) Larger grogs decrease the strength of the mixture both in the green and fired state. A mixture of

clay and fine grog will stand load much better than a mixture of clay and coarse grog. Coarse grog makes the product brittle and fragile.

(3) The larger grog greatly increases the resistance to sudden temperature changes during firing and cooling.

(4) Fine grogs give higher porosity than coarser ones but at high temperature vitrification sets up rather rapidly with fine grog.

In order to bring compromise between these effects it is customary to use a combination of different grades of grog particles which vary according to the nature of work to be done with the refractory goods.

Grogs should be similar in composition to the raw clay used with them, and should be previously fired at as high temperature as possible. In the Continent special grogs are made by burning fire clays usually at about 1400°C and sold as *chamotte*.

The term grog generally denotes powdered burnt clay but this term is also used in many instances to denote powdered silica or calcined bauxite etc.

Refractories.

Refractories are articles made of refractory materials mentioned before. The various refractories used in pottery industry may be mentioned as follows :—
Refractory bricks, saggars, muffles and crucibles.

Bricks. These are mostly made from fire clays and known as fire bricks. In special cases highly siliceous materials such as pure sand, powdered quartz, quartzite or kaolin waste are used for making what are

known as silica bricks. Special refractory materials such as chromite, bauxite, graphite or carborundum are often used for making bricks for some specific purposes as already mentioned before.

Uses. Refractory bricks made of fire clays are chiefly used for the constructions of furnaces, kilns, flues and boiler settings etc. Semi-silica bricks are mostly used for the constructions of crowns and arches of furnaces, cupolas and crucible kilns, where constancy of volume is a main factor. Semi-silica bricks are more readily attacked by slags or other chemically active materials specially of basic character. They are largely used in coke ovens. Semi-silica bricks are always less refractory than good fire clay bricks or silica bricks as additions of sand, ganister or silica rocks to a good fireclay always reduces the refractoriness of the clay or the silica. Pure silica bricks specially lime bonded ones are chiefly used where great heat resistance and absence of shrinkage are the main criterians. They are extensively used for the upper parts of glass tanks, for the hottest parts of gas fired furnaces and kilns, reverberatory furnaces and coke ovens. Fire clay bricks are less suitable for these purposes as they shrink on heating and tend to fall down on prolonged use, but these bricks can stand rapid changes of temperature much better than silica or semi silica bricks.

Graphite, plumbago or carborundum bricks are chiefly used in the partition walls of chamber kilns, coke ovens and muffle furnaces where heat conductivity and resistance to sudden temperature changes are

required. These bricks show greater resistance to the corrosive actions of slags both acidic and basic and are often used for smelting copper, lead, aluminium and steel. Chromite bricks are neutral in character and used for the same purposes as carbon bricks but chromite bricks have much greater mechanical strength than the carbon bricks.

Basic bricks made from magnesia and dolomite are used where high refractoriness is required together with great resistance to metallic oxides and slags of basic nature. The chief use of these bricks is in the iron and steel industry for lining the furnaces and converters. Magnesia bricks have replaced dolomite for this purpose; as the latter is not so durable. Magnesia bricks are excellent for gold, silver and platinum refining furnaces and for smelting lead, antimony and copper ores. They are also used in cement rotary furnaces. Zirconia bricks are used for the same purposes as magnesia ones but the former are more refractory and best suited for the roofs and arches of electric furnaces. Bauxite bricks are better suited for rotary cement kilns and in lead refining furnaces than magnesia bricks. When well made they are exceptionally resistant to corrosion.

Fire clays used for making bricks are often weathered before use. It makes the clay more open and homogeneous so that the clay mixes better with water and passes evenly through machines. It has been observed that for many purposes fire bricks can be better made from a mixture of two or more clays which will have the requisite properties. In addition to fire

clays, it is also advisable to use a certain amount of grog in order to keep the shrinkage of the clays within proper limit. Fine grained grog dissolves in the vitrified flux more easily than coarse grained ones, producing a body of very close texture making the bricks liable to dunt or shatter at sudden changes of temperatures.

During firing, the more fusible constituents of the bricks, form a matrix, binding the other materials together. This matrix, particularly in the coarse grained materials, seems to determine the refractoriness of the fire bricks under load. The flux or matrix which binds the coarser constituents of the bricks together is quite different in the grog, from what it is in the clay, even though the grog is made from the very same clay. This is due to the fact that in the grog the fluxes of the clay have dissolved so much of the less fusible constituents, that the fluxes have become more viscous and less fusible than those of the original clay. When the clay and grog are fired together, the fluxes of the clay soften earlier than those of the grog and do their respective works independently. By thoroughly burning the bricks at a high temperature, the binding matrix is stiffened so that it cannot dissolve any more less fusible constituents, and the resulting fire bricks become more refractory under load. Semi-silica bricks are sometimes made with kaolin wastes, but as these materials often contain fusible impurities such as particles of feldspar and mica, the bricks are of second quality. The shrinkage of these bricks is very low due to their high silica content.

Making. The common method of making fire bricks is to grind up the fire clays and broken bricks together in edge-runner mills, but this is not a very satisfactory method for high class bricks. For superior class of fire bricks the clays are ground separately and mixed in desired proportions with grogs of different sizes made previously. The mass is then delivered into the mixer where suitable amount of water is added, to make it plastic. From the mixer the mass falls into a pugmill, either vertical or horizontal, the latter being preferable, as it consolidates the product better.

If the fire clay is stiff, the mixed mass before being sent to the pugmill is kept for a day or more in a soaking pit so that the mass is thoroughly and evenly soaked with water to facilitate subsequent treatment.

There are various machineries for making bricks, but hand moulding is still in use and it is believed by some people, that hand made bricks are superior to machine made ones, as the latter are made with greater force and consequently become more dense. Internal strain set up in hard pressed bricks sometimes become serious during subsequent use. Hand presses are often used to make clay bricks when clearness of shape and accuracy of size are essential; but the rate of production is slow.

In Great Britain very stiff pastes are used for making hand moulded bricks. A skillful worker can make 200-250 hand moulded bricks per hour with the assistance of one boy only. These bricks are so accurate that they require no repressing. In America

it is customary to use softer paste for hand moulded bricks but these bricks require to be repressed to give them accuracy of size and shape. A moulder with two boys in America generally make about 400 hand moulded bricks per hour. These bricks when they are partially dry are sent to the pressers where also one man assisted by two boys press about the same number of bricks per hour as made by the moulders.

For moulding bricks by machineries there are three processes in general practice. The plastic moulding, the stiff plastic, and the semi-dry pressing. In the plastic moulding a soft mass of clay is used as in the hand made process. The most common practice of this method is the wire cut process. In this process the plastic paste, thoroughly mixed previously in a mixer, is put into a pugmill having a mouth piece through which the clay extrudes in a continuous band which has the shape and size of the bricks that are to be cut from it. This band is cut by a wire into pieces sufficiently long for making six bricks at a time. These sections are then again cut into pieces equal in dimensions of the bricks by a series of wires stretched tightly in a frame. In this manner bricks are produced, six or more at a time and are taken away on boards to be dried. These bricks after drying to certain extent may be pressed when greater accuracy of shape is required.

In the stiff plastic method coarsely ground fire clay and suitable amount of grog and water are treated in a tempering mill to produce a somewhat soft mass.

This mass is then taken to a trough mixer and the finer portion of the fire clay is mixed with the mass to produce a stiff plastic paste. This paste is then passed through a pugmill and then shaped into bricks in special machineries. In this process the plasticity and the peculiarities of the fireclay are fully developed yet the paste is not so soft as to make the pressed bricks warp or shrink much during drying. Not too high pressure required in this process avoid those defects in bricks caused by excessive pressure during moulding.

When the bricks are made by the semi-dry process, a very powerful press is required. In this process the material is used in the form of powder which contains just sufficient moisture to make the powder to cake. This moisture which does not exceed 10 per cent in most cases is best applied by steaming as liquid water is difficult to distribute evenly. It is generally used with shales and dry clays which are almost devoid of plasticity. Several types of press are in use for this purpose which can render high pressure on the material in succession, as a single pressure, however great will not produce a sound brick. It is necessary to press the bricks in succession in order to allow the air to escape before a compact mass can be formed. Bricks made by this process have got greater accuracy of shape, less shrinkage and give much better results on crushing but they are less resistant to abrasion and the corrosive actions of slags or flue gases than the bricks made by the stiff plastics process. When clays are tempered

with water and then subjected to high pressure a surface skin is developed on the bricks which protects them from easy abrasion.

Drying. Bricks made by the semidry pressing contain so little moisture that they are taken directly to the kiln. Ordinary hand pressed bricks contain from 20 to 25 per cent of water. The moisture content of bricks made by other processes generally vary from 5 to 15 per cent according as they are made by the so called dry process or in the stiff paste condition. Otherwise speaking, with a moisture content of about 20 per cent, no less than seven tons of water must be removed in drying 10,000 bricks of normal size.

Bricks are generally dried in the open air in common brickyards specially where moulding by hand is in practice. The bricks as they come out of the mould, are laid flat on the ground previously prepared and dusted with a thin layer of sand. When they have hardened sufficiently, they are piled up in a heap, keeping sufficient space between each brick for the circulation of air. These heaps or stacks are generally erected on the higher parts of the ground as the speed of drying at the height of ten feet is about double of that on the ground itself. When there is any fear of rain the stacks are covered with straw mattings or other moveable light coverings.

In bigger brickyards special drying sheds are erected in order to hasten the progress of drying and to get a larger output in a shorter space. Various artificial driers are designed for this purpose but it seems

hardly likely that those would be advantageous in the tropical countries like India where bricks can be dried cheaply even in moist seasons on shelves suitably arranged. Heated drying sheds are very suitable for countries where sunshine is rare, and various devices are made in the western countries to utilise the waste heat from the kilns. The drying can be greatly improved by arranging fans in suitable places along the drier to keep up a regular artificial draught.

Properties of Fire bricks. These are mainly dependent on the materials of which the bricks are made but the treatments of the materials during making and firing are also responsible for the final properties of the bricks. The more important properties of fire bricks may be summed up as follows.

Refractoriness of fire bricks depend on the conditions under which they are tested. The minimum temperature of softening of a refractory brick is Seger Cone 26 or 1580°C when heated in an oxidising atmosphere, the temperature rising slowly at a rate of ten degrees per minute. The better class of refractories should not show any sign of fusion below cone 30 or 1670°C .

The resistance to prolonged heating depends mainly on the composition of the brick. Silica bricks collapse somewhat suddenly when the softening temperature is reached but fire clay bricks collapse much more slowly. The main reason is attributed to the formation of sillimanite or mullite crystals when fire clays are subjected to prolonged high temperature. If a fire brick is not sufficiently fired by the maker it would

contract or expand during subsequent use according as it is made from fire clay or silica respectively. *After contraction or expansion* of fire bricks is tested by heating a test piece ($3'' \times 2'' \times 2''$) to a temperature of 1410°C (Cone 14) in two hours and maintaining it at that temperature for another two hours in an oxidising atmosphere. The test piece shall not show an after expansion or contraction of more than one per cent.

Texture of fire bricks has got more importance than is ordinarily understood by the users. Bricks with coarse texture are less sensitive to sudden temperature changes than fine textured ones while the latter can resist the actions of slags and flue gases longer than those of more open and coarse textured bricks. The surface texture or 'skin' of fire bricks often resist the action of slags or flue dust. This skin is formed when bricks are made under high pressure as some of the finest particles of clay are carried on to the surface forming a thin but dense layer. While the interior of the brick is more porous. A dense hard skin increases the resistance, to abrasion of the brick which is very important for specific purposes.

A comparative study of common flue-ash and the slag formed on the surface of fire bricks inside kilns show that the slag is not very different from a mixture of a very small amount of the refractory bricks with a very large amount of the flue ash. The hot dust from fuel-ash gets deposited on the brick surface forming a glassy coating, which on further heating begins to dissolve little portions from the bricks and finally

trickles down the sides of the kiln walls. Thus the bricks get gradually eaten away specially if the brick surfaces are not compact enough to hinder the easy penetration of the glassy fluid.

The texture of fire bricks shall be regular, containing no holes or flaws. All surfaces shall be reasonably true and free from winding, or spongy spots. Fire bricks generally have porosity not less than 12 per cent by volume or 6 per cent by weight.

Crushing strength or hardness of fire bricks is mainly due to the amount of cementing material formed to bind together the other infusible particles. This cement is formed by the fusion of the small amounts of fluxes present in the raw materials, the formation of which is directly related to the temperature and duration of firing of the bricks and the pressure during making. Cold crushing strength of fire bricks is in most cases much more than what is actually required but in any case it should not be less than 1800 lbs per sq. inch.

As fire bricks are mainly used in high temperature furnaces and kilns, the crushing strength of the bricks at the highest temperature in actual use is more important than their strength when cold. It has been shown by Bodin that some fireclay—alumina bricks show their greatest strength at about 1000°C but as the temperature rises up the crushing strength diminishes rapidly. The softening of fire bricks under a load may be attributed to some extent, to the fact that the small amount of fluxes present undergoes

rapid chemical combination with the finer particles when the brick is under a pressure, this reaction taking place rather slowly in normal condition of pressure. The presence of fluxes is not the only cause of the weakness of fire bricks. Watt suggested that the failure of some fire bricks at about 1200°C is due to the rapid crystallisation of sillimanite so that the bricks fail suddenly when subjected to a load. Fire clay bricks should not show serious deformation when heated to cone 12 or 1350°C under a load of 25 lbs per square inch. Silica bricks under similar pressure should stand a temperature of 1580°C or cone 26.

Spalling. When a fire brick gives way under sudden temperature changes, it is often found that the cracks are formed along one or more well marked lines and as a result pieces come off bodily. This phenomenon is called spalling of fire bricks. The texture of the brick has a great bearing on the tendency to spall. An open texture brick would spall much less than a closed one. Fire clay bricks are much stronger in this respect than silica bricks. The test is done by heating a brick previously weighed, to a temperature of 1350°C and then exposing it to a blast of cold air for a period of 15 minutes. The test is repeated for ten times after which the brick is reweighed. A good fire clay brick should not show a loss more than 12 per cent by spalling. Magnesia bricks are completely destroyed under similar conditions.

Saggars. Saggars are fire clay boxes of various shapes and sizes, but they are chiefly made in round

or rectangular forms. They are used for holding clay wares during firing, in order to protect them from the direct contacts of the flames and the fire gases.

Saggars are perhaps the most important refractory wares that are used in the pottery manufacture. They are usually made of fire clays, with the addition of some opening materials such as grog.

The proportion of grog should be as large as possible, consistent with the necessary strength of the article, and the plasticity of the clay used ; as this keeps the burnt saggars open, allowing it to withstand sudden variations of temperature and minimise the contraction. The materials from which the grog is made should also be properly fired so that the grogs do not contract any more when mixed with the clay for making new saggars.

In making the saggar mixture with clay and grog, it is advantageous to use two different kinds of clays,—a fat or plastic one, and a lean or sandy one. The proportions of the two varieties are to be determined by trial in each case. The amount of grog commonly used in saggar mixtures is from 50 to 60 per cent. The following formula would give a good mixture to start with.

Fat or plastic clay	30
Lean or sandy clay	17
Coarse grog	20
Medium grog	33

Fine grog is used in making small saggars for holding plates and other flat wares both, china and porcelain.

The grog and the clays are first spread in dry state in layers, one on the top of the other. They are then repeatedly mixed with sprinkling of water. This mixing is also made in mechanical mixers where water is added in a spray. The mixed mass is then thoroughly kneaded and pressed, by passing it once or twice through a pug mill. This mass is then piled up in a heap in a cool place and allowed to stand for several days or weeks for ageing.

Saggars are usually made by one of the following processes.

Hand moulding. In this beating the ring or the side of the sagger is first made by beating a slab of the mixture, on a table dusted over with fine grog, on which are fixed four iron rules the thickness of which is equal to that of the slab. The mixture should be firm enough to be shaped by striking with a wooden hammer. The bottom slab of the sagger is then similarly made and cut into proper shape. The slab for the side is then lifted and rolled round a wooden mould placed on the bottom slab, and the junction between the bottom and the side slab is then carefully pressed together by means of a wooden knife. The mould is then taken off, and the inside of the sagger finished in the similar way. It is a practice in England, that the mixture to be used for the bottoms of saggars is made with more grog than that used for the sides. A man

can make 40 to 50 saggars in a day by hand moulding.

Machine pressing. This process has the advantage of making saggars of almost any shape and size. The mixture should be properly made with less water in order to press well. A reasonably short body gives better result than a fat one. The only disadvantage of this method is that the bottom of the saggars are more densely pressed than the sides, resulting in unequal strength of the saggars. To minimise this difficulty, it is customary to press only those saggars which are not more than 3 to 4 inches high. Higher saggars when pressed similarly, generally crack at the sides after the third or fourth firing. A man can make about 300-400 saggars three inches high, per day, in a power driven machine.

Jolleying. Only round saggars can be made by this process, and the mixture used must be soft enough to allow the profile to do its work. The moulds used for this purpose are generally made in two parts. The ring, which is generally 1 to 2 inches in thickness depending on the size of the saggar; and the bottom, which is slightly curved upwards, in order to make the lower end of the bottom a little arched, which is believed to give strength to the saggar bottoms. The jolleying is done in the usual way, but the moulds are dusted every time with fine clay dusts, generally sweepings from pressing shops, in order to facilitate the delivery of the wet saggars from the plaster moulds. The profiles are supported on the inner side by wooden blocks about an inch thick, to give them more strength.

Casting. Sometimes saggars are made by casting in plaster mould like glass house pots. Larger proportions of grog can be used in the casting slip treated

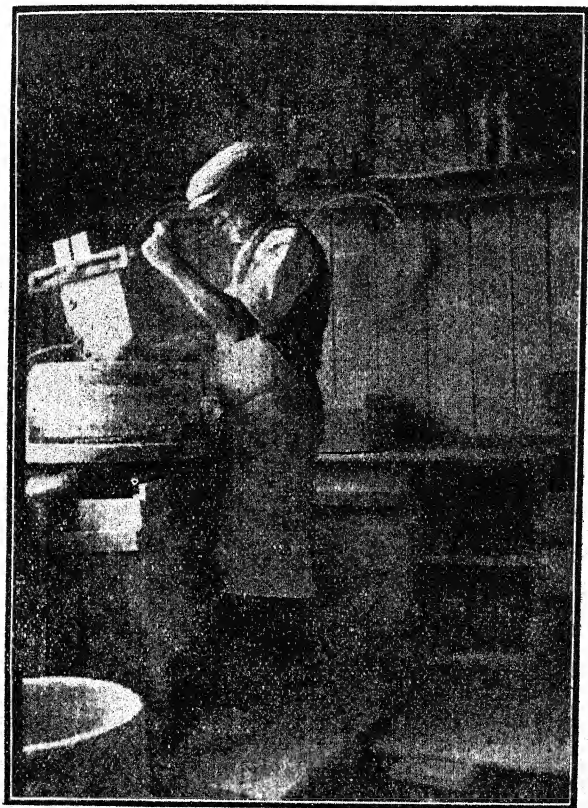


Fig 26. Sagger making by Jolley.

with alkalis, with the consequent increase in the refractoriness of the saggars, but the cost of production is not so favourable with this method of production.

Saggars are dried on wooden racks, placed either on plaster bats or iron plates. In the Continent where two-chamber kilns are used, racks are generally erected round the second chamber and the waste heat from the ovens is conducted through large pipes and distributed throughout the racks for drying the saggars. In England where one-chamber ovens are in use, special saggar rooms are made, heated with the waste heat from the boilers. Saggars should not be dried too quickly other wise very fine cracks may be formed which may afterwards expand during use.

Saggars are burned in the same oven in which the wares are fired, but the green saggars should be burned empty. In the common one-story ovens, the upper bungs or the top most parts of the oven space are used for firing green saggars, but in the Continental two-stage-ovens, the upper story is chiefly filled with green saggars, either empty or with light articles. This method of saggar burning, though economical in cost, is not so satisfactory, as the saggars are only incompletely burnt and may get twisted and chipped off, if not carefully handled.

Saggars, that are to hold glazed articles specially with lead glazes, are usually coated internally with a thin glaze wash, in order to prevent the porous saggars from absorbing the glaze from wares placed in them. For this purpose, the cleanings from the glaze tub is generally used. This glaze washing of the saggars also prevents little fragments from falling

upon the wares in the saggars below them and also helps to make the saggars last longer.

Saggars should not be kept in a damp place or allowed to absorb damp by any means. At the first stage of firing, the steam evolved from the sides of damp saggars liquid condenses on the cooler wares inside. This is not pure condensed water, but also carries with it some sulphurous vapours derived from the fuel gases. As the temperature rises, this condensed water evaporates from the surface of the wares, but not before doing some damages which may show themselves as flowing of the decoration, or in sucking of the glaze specially at the edges and bottoms of the wares, producing eggshelly effects.

During constant use of the saggars, damages are caused in the form of cracks along the sides or chipped off edges. These damages must be mended carefully whenever they are detected. The best cement for this purpose can be made by mixing suitable proportions of grog and waste glaze or water glass. A little amount of china clay may be added to make this mixture a little plastic, but too much clay would cause the mixture to shrink and the joints would easily fall out. When using a cement containing water glass, it should be remembered that this material requires a fairly high temperature to harden it properly, and the repaired saggars must be fired before they are used.

It is very difficult to give any definite idea of the life of saggars. They may last from 3 to 25 firings according to the conditions in which they are used.

Saggars which in ordinary work lasted some 15 firings were found to last 8 to 9 firings when the work was rushed through. In tile works where firing and cooling are much more gradual than in general pottery works, saggars are seen to last some 25 firings. In some Continental porcelain factories where very high temperatures are used, saggars are found to last only 3 firings. The average life of saggars is calculated to last some six firings in white ware factories.

Some saggar materials. Carborundum has been suggested by several authors as a very satisfactory material for making saggars, but it has been shown by others that equally good, if not better, results can be obtained from fused quartz at much lower cost and suffering no reduction effect like carborundum. It can also be used as grog with any clay. It is more economical to substitute mixture of ball clay and china clay, for fire clays or marls. The higher the temperature of firing, the less amount of ball clay should be used. Addition of fused quartz about 50-60 per cent, produces saggars almost proof against dunting due to rapid cooling and heating, with suitable clay mixtures. Saggars which contain fused quartz, should have a dead ring, as those saggars that ring well, invariably dunt more readily than those with dead ring. H. Thie mecke (1934) found that when about 15 per cent of talc is mixed with a normal saggar body, it increases the mechanical strength of the saggars both in dry and fired conditions and decreases the total shrinkage and

coefficient of expansion. The wares have smoother surface and can stand heat changes much better.

Muffles. Muffles are refractory boxes or chambers used for heating goods out of contact with flame or other products of combustion. Muffles serve the same purpose as saggars but unlike saggars they are built more or less permanently inside a furnace. The muffles are made of various sizes, the smaller ones being made in one piece with a flat bottom and arched top. Larger muffles are generally made in sections with special refractory bricks or tiles, the joints overlapping each other in order to prevent the gases from the furnace from entering into the chamber or the muffle.

As the heat from the furnace enters into the muffle chamber by penetrating through the walls, the latter should be as thin as possible consistent with the strength required and the material of which the walls are made should have a high heat conductivity. Walls of large muffles made of bricks are $4\frac{1}{2}$ inch thick while small muffle walls are made $\frac{1}{2}$ inch to $\frac{3}{4}$ inch thick.

The chief properties required of a good muffle are (1) resistance to sudden temperature changes; (2) good heat conductivity of the walls and; (3) strength of the base while hot. The first property is obtained from a proper mixture of fire clay and grog. A more porous material can stand sudden temperature changes better than a dense one. The heat conductivity of a fire clay can be greatly increased by mixing graphite, carbon or carborundum with it. When using these materials, the outer surface of the muffle walls should

be covered with a thin wash of fine fire clay so that the carbonaceous materials may not get oxidised easily. For small laboratory muffles fused quartz is very useful. These muffles can be heated easily and cooled rapidly without any danger of cracking. Muffles made of fused quartz are perfectly impervious to furnace gases which is not possible with muffles made of fire clay and grog. Special care has to be given in making the base of small muffles which are made of one piece. The base should be so strong that it does not give way under the load of the articles on it when the whole muffle is at a very high temperature. A judicious mixture of fine and coarse grog increases the mechanical strength of the base. A small amount of carborundum increases the mechanical strength to a great extent. Before mixing the clay with the grog the latter should be soaked in water so that the final mass remains more porous which is so very essential for muffles. Proper souring of the wet mass ensures better working property and less chance of cracking of the joints of the muffle during drying period.

Making. Small muffles are best made by hand on wooden cores. The plastic mass is first battled flat to proper thickness on a wet jute cloth which is then wrapped round the wooden core or frame. The cloth is removed and the two ends of the flat mass joined and trimmed with a wooden tool. The back portion of the muffle is then joined in the same way. Too much water should be avoided in joining the ends to prevent

cracking during drying. When the clay has dried to some extent the wooden frame is taken out and the muffle allowed to dry slowly on its closed end over a perforated rack. Small muffles can be made by casting like saggars. Mechanical devices are sometimes used to make the hollow portion of the muffle, the closed end being joined afterwards by hand.

Great care should be taken in drying small muffles which are liable to twist or crack on rapid or unequal drying. Fine cracks which may develop during drying are not noticeable before the muffle is fired when it is too late for any remedy. In a hot country the first stage of drying should be in a cool place preferably an underground cellar. Later on the drying can be made on a hot rack or direct in the sun.

For firing, the muffles are stacked one above the other like saggars in a low down draught oven and fired to a high temperature. They can also be fired conveniently on the top portion of an ordinary pottery oven like firing of green saggars.

Crucibles. These are semi-cylindrical open top vessels made of very refractory materials and used for smelting frits for glazes and enamels or melting metals or alloys. They are made of various sizes beginning from the smallest laboratory crucibles to the largest ones used for melting iron, copper etc. The laboratory crucibles for chemical analysis are made of highly refractory chemical porcelain where as small cupolas used for assaying gold or silver are made of bone ash. The latter substance has property of

absorbing the oxides of copper, lead etc. which are often found as impurities in gold and silver, where as the molten silver or gold are not absorbed by the vessel made of bone ash.

Apart from the high refractory property required from these crucibles, they must stand sudden changes of temperature when they are taken out of the furnace and their hot fluid contents emptied out. The material of which the crucible is made must be able to resist the chemical action of the hot molten substance melted in the crucible and for this reason great care should be taken in selecting proper crucible for a particular purpose.

Various crucibles according to the raw material used for making them may be broadly classified as :—

- (a) Fire clay crucibles
- (2) Plumbago crucibles and
- (c) Special crucibles.

For all general purposes specially for smelting glazes and enamels fire clay crucibles are most common. They are very refractory and can stand the corrosive actions of most of the molten materials, but these crucibles are not so insensitive to sudden temperature changes with the result that they can not be used repeatedly. Common fire clay crucibles are made from highly refractory fire clays mixed with about 25 per cent of grog made of the same clay. When plastic ball clays are also used with fire-clays the amount of grog may sometime be increased to 50 per cent as in *London crucibles*. Sometime free sand is mixed with fireclay to produce crucibles of siliceous type like

Hessian crucibles. These crucibles are used for melting gold, silver and other precious metals. These crucibles generally contain equal amounts of free silica and clay. The clay must be very plastic for proper binding.

Plumbago crucibles are very resistant to sudden temperature changes and highly refractory. Carbon being neutral to chemical actions, almost all metals and alloys can be melted in it. The heat conductivity of these crucibles is also high. The only draw back of these crucibles is that they get easily oxidised unless the surface of the crucible is protected with a thin coating of very fine fire clay. If five to eight per cent of graphite or gas carbon is mixed with ordinary fire clay crucibles it improves the refractoriness and resistance to sudden temperature changes of the fire clay crucibles to a great extent. These mixed crucibles are often used for pure steel and other sensitive alloys like brass when high carbon is injurious. Ordinary plumbago crucibles are made of one part of a very plastic fire clay and two to three parts of graphite or coke powder by weight. These crucibles are largely used for melting cast iron, mild and hard steel, copper etc.

Special materials like alundum or fused alumina, carborundum, chromite, zirconia etc. are sometimes used in making special crucibles for specific purposes, to stand very high temperature of firing.

Alundum crucibles are extremely refractory and have high thermal conductivity. Due to their high

cost these crucibles are not used in general industrial purposes.

Fused silica crucibles are very useful when the molten mass is not of a basic character. These crucibles are smooth, non-porous like porcelain crucibles, and due to their greater insensitiveness to sudden temperature changes than porcelain, the latter is being gradually replaced by the former in general laboratory work.

Making. Refractory crucibles can be made by all the various processes by which round shaped clay-ware are made. These are (1) casting in plaster moulds (2) jolleying (3) throwing on potters wheel (4) pressing in a mechanical press and (5) hand moulding.

When the clay or the body mixture is not very plastic the process of casting is very suitable for making crucibles. Highly plastic clay mixture can not be cast satisfactorily. The clayslip is made in the usual way by the addition of very small amount of soda silicate and soda carbonate so that the slop weight is about 36 ozs. per pint. If the clay contains soluble sulphates or chloride a small amount of barium carbonate may be added to precipitate them before the proper electrolytes are added as these salts when present in clays interfere with the action of the alkalis. When very large number of crucibles are to be made the process of jolleying is a good one, but this process is not to be recommended for larger sized crucibles. As the clay paste used for jolleying is to be very soft, the sides of the crucibles remain very open which is not so desirable.

When larger crucibles of special shape are required, throwing is recommended. This process is rather costly as only very skillful and responsible workmen can be relied upon for this task.

Pressing on a hand press or a power driven press is generally used for crucibles of small and medium sizes. Big crucibles made by this process suffer the same defects as described in the case of saggars. There are various types of crucible press placed in the market with their respective drawbacks. A modern power driven press can make about 750 crucibles per hour of six inches diameter, when helped by two men.

For making the largest crucibles, hand moulding seems to be the best process. In this method the crucibles are made either on inverted wooden cores as in the case of making small muffles or they are made in steel moulds by means of a hand worked plunger made of steel. As the bottoms of crucibles are thicker than the sides, this portion is first worked up on the top of the wooden core and then the side gradually developed by hand to the required thickness. In some cases the wooden core is placed on a rotating vertical spindle and the crucible shaped by means of a wooden tool. In the steel mould process the lump of clay mass is put inside the mould and then shaped with the steel plunger with a rotating movement by hand.

The drying and firing of the crucibles are done with the same carefulness as in the case of small muffles.

CHAPTER X.

FUELS, FURNACES AND KILNS.

Fuels. These are materials used for producing heat. They must ignite with comparative ease producing as high temperature as possible. Fuels that are largely used for general industrial purposes are regarded to be derived primarily from cellulose and they may be conveniently classified as follows :—

Forms	Natural fuels	Artificial fuels
Solid	Wood, peat, lignite or brown coal, bituminous coal, anthracite.	Charcoal, coke, brickets.
Liquid	Petroleum oil.	Distilled oil from coal tar, shales etc. Spirits.
Gaseous	Natural gas.	Coal gas, coke-oven gas, producer gas, oil gas.

Solid Fuels.

Wood is the universal fuel since mankind learnt the use of fire. Since it contains much moisture (20%) even when air dried, its calorific value is low, so it can not be used for high temperature work. But it is readily inflammable and burns with a fairly long flame producing less soot and ash; when heated to 160°C or more out of contact with air it forms *charcoal*. As a fuel charcoal has higher calorific value. When dried artificially wood is a good fuel when found cheap.

Peat consists of partly decomposed vegetable matter of lower forms of plant life, mostly mosses, which have lost their vegetable characteristics and have become semicharred—brown to black masses. When freshly dug peats contain sometimes as high as 90 per cent water and when air dried, contain about 20 per cent water. Peats vary in composition usually containing much more ash than wood and have lower calorific values.

Lignites hold an intermediate position between peat and coal. They vary very widely both in physical character and in chemical composition. The better varieties are known as Brown coal and largely used in the Continent of Europe and in Assam and South India. The water content varies from 40-60 per cent before air drying. Dried lignite is hygroscopic in character. In the Continent lignites are converted into *brickets* by pressing the powdered lignite mixed with coal tar pith as binding agent. The artificial brickets are not so hygroscopic and

have greater calorific values than the original lignites from which they are made.

Bituminous coals contain the largest amount of volatile hydrocarbons which burn with a long yellow flame. It has been ascertained that coals having the medium volatile content of 16-20 per cent have the greatest economic efficiency. With too high volatile matter gases escape unburnt, on the other hand, with low volatile matter an excessive air supply is required for the fuel on the grate. Since bituminous coals burn with a long flame and high temperature, they are very much suitable for pottery and glass furnaces. The amount and fusibility of ash in coals are important factors to be considered when selection is made.

Average composition of solid fuels.

Materials	C	H	O&N	Calorific value.	Ash.
Cellulose	44.4	6.2	49.4	4150	
Wood (Dry Oak)	50.16	6.02	43.4	5035	0.37.
Peat (Dry)	57	6.1	34.9	4500	5-10.
Lignite (Dry)	56.85	5.7	10.37	5000-7600	5-10
Bituminous (Coal)	82	5	13	8500	10-20
Anthracite	90	3	3	8800	9-15
Coke	89	0.5	2.5	7000	10-14

Average composition of Indian coal.

Coalfield.	Fixed carbon.	Volatiles.	Moistures	Ash.	Remarks.
Jharia field	56.8	28.1	1.7	15.1	Ash varies from 12-21
Daltongunj (Behar)	42.00	30.90	6.60	19.50	
Central Province.	45.80	34.50	4.50	15.2.	The Composition varies widely. Calorific value 5700.
Umaria (C.I)	66.71	19.71	5.46	8.12	
Talcher (Orissa)	44.11	35.65	11.33	8.91	
Singerini (Hydrabad)	56.50	25.25	7.60	10.65	Iron pyrites present in appreciable quantity.
Assam.	48.99	43.58	3.19	4.24	3.14% S
Punjab.	40.00	37.00	9.00	10.00	4% S
Baluchistan.	46.52	41.51	2.28	8.84	Sulphur 2 to 3 %
Raniganj field (Bengal)	54.95	33.95	2.57	11.1	

Anthracite coals contain the lowest amount of volatile matter and high proportion of fixed carbon. They produce an intense local heat, and short flame. They are not so suitable for high temperature furnaces particularly for ceramic industries. They are mainly used in the metallurgical furnaces, in crucible furnaces and for the production of water gas.

Coke is the residue left after heating coal out of contact with air. It contains all the ash of the coal less a small proportion which has been volatilised. Good coke for furnace work should not contain less than 85 per cent C and the ash should not exceed 10 per cent. It is used for heating crucibles and other article requiring direct heat.

Liquid Fuel.

The liquid fuels used for industrial furnaces are, the heavier portions of natural petroleum and the distilled oils from tar and shale. The principal characteristics of these oils should be :—

(a) It should have a high heating value. The heating value of a fuel oil can be approximately determined from the sp. gr of the oil by Sherman and Kroff equation.

Heating value in B.T.U per pound of fuel oil.

$$= 18,650 + 40 (\text{Baume reading} - 10)$$

In general, oils which are lighter in sp. gr. give higher calorific value.

(b) It should have a high flash point. If the fuel oil ignites at low temperature, there is danger of spontaneous ignition of the oil. The flash point of these oils should be above 60°C .

(c) It should not be too viscous or become sluggish to flow at 0°C . The viscosity of a fuel oil decreases considerably with the rise of temperature. Oils having the same specific gravity but obtained from different sources are often found to have different viscosities. Too viscous oils do not flow properly into the burners unless they are preheated.

(d) It should not contain much sulphur (reject if above 1 p. c.), water (reject above 2 p. c.) or solids e.g. sand, clay or dirt, not more than a trace.

Petroleum occurs widely distributed throughout the world. As obtained from the borings it varies in colour from light yellow to almost black. The sp.gr ranges from 0.77 to 1.06. Chemically these oils consist of mixtures of numerous hydrocarbons. Two outstanding types of petroleum are generally met with: (a) the paraffin base oils and (b) the asphalt base oils. The latter are more viscous and darker in colour. The crude oils used for external combustion are derived from these natural oils after removing the lighter fractions by distillation.

The lighter fractions are used in the internal combustion engines and lighting purposes. The percentage yields of heavy fuel oil vary widely with different sources of petroleum. American petroleum yield about 20 per cent of heavy oil used in industrial furnaces

where as petroleum from Borneo yield as much as 75 per cent heavy fuel oil.

Shale oil. Some shales specially of Scotland, New South Wales and New Zealand yield on distillation from 18 to 40 gallons of crude oil per ton of shale. This crude oil is first separated from the valuable lighter products e.g. motor spirit, naphtha, lubrication oil etc. and then used as fuel oil.

Tar oils. These are obtained from distillation of coal tars. After removing the lighter fractions and the pitch, the product is used as fuel oil.

The various products that are obtained at different temperatures by the distillation of coal tar are given below.

1. Light oils, (up to 170°C) yield motor Benzole etc.
2. Middle or carbolic oils ($170-230^{\circ}\text{C}$). Tar acids removed by alkalies. Napthalene also separated.
3. Cressole oils ($230-270^{\circ}\text{C}$). Used as wood preservative and disinfectant.
4. Anthracene oils ($270-320^{\circ}\text{C}$). Crude anthracene removed.
5. Pitch. The fractions 2-4 are commercially known as Tar oils and may be used as fuel.

Average compositions of different fuel oils.

	C	H ₂	O&N	S	Calories
Petrol Oil	84.5	12.5	2	0.5-1.0	10900
Shale Oil	87.5	11	1.5	0.4	10600
Tar Oil	87.89	65.75	3.5	0.5-1	8900

Atomisation of liquid fuel.

When a liquid fuel is set on fire, it burns at the surface with a yellow sooty flame. If this sooty flame comes in contact with a comparatively cooler wall of the furnace, a deposit of black carbon is formed on the wall. If the oil is vaporised or atomised and thoroughly mixed with air the combustion is quick and complete and there is no chance of deposit of solid carbon against the walls of the furnace. The oil is vaporised by highly preheated air passing through a recuperator or a regenerator but the atomisation is done either by steam or air under pressure.

Ordinary liquid fuels, with the exceptions of light distillates, leave some residues during vaporisation which means that the vaporiser must be cleaned at intervals. For this reason vaporiser burners are seldom used in continuous industrial furnaces. The control of these burners are also not very satisfactory.

All the important oil burners specially for ceramic furnaces and kilns are based on atomisation of the oil which means fine subdivision or spraying of the oil. The oil is supplied to the atomiser from a feed tank placed at a sufficient height to give the necessary flow.

There are various types of oil burners but they are made more or less on the same principle.

The general principle of these burners is that the oil and steam or air are injected through concentric orifices so that the oil is efficiently atomised and thoroughly mixed with air for proper combustion. If the

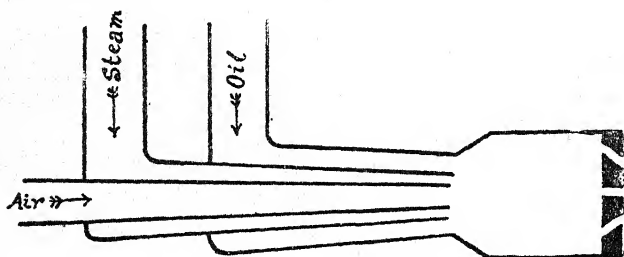


Fig. 27 Holden Atomiser with steam.

oil is too viscous specially in cold weather, it is heated in the tank with steam coils. These burners are so constructed that they can be easily taken into pieces and cleaned from time to time.

In the *Holden burner*, oil is fed by gravity into the outer annular ring, steam being led in immediately inside this tube. Owing to the injector action of the oil and steam, air is drawn in through the central tube.

Oil spray, steam and air get mixed at the larger chamber at the fore-end of the burner and the mixture is forced out through the orifices at the front plate bored at different angles so that the air, oil and steam get again mixed up thoroughly. This type burner is generally used in the locomotive and marine boilers.

In the *Carbogen system* two air streams impinge on the oil from both sides atomising the oil efficiently which then gets mixed up with the air. This type

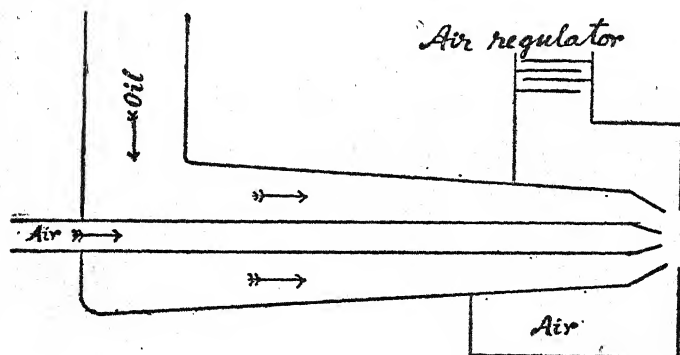


Fig. 28 Carbogen atomiser with air.

of atomisers are generally used in glass furnaces for generating flame of high intensity without the deposition of free carbon.

Wade burners can be used with air or steam and is largely used in England for pottery kilns.

Air atomisers consume only half the amount of steam (for the compressor) required for direct steam atomisers. The relative efficiencies according to Kermode are :—

Steam. 68-75 p. c. Air. 78-83 p. c.

Pressure required for air atomisers vary with the pattern. Generally a pressure between 20 to 30 lbs per sq inch is sufficient.

When steam atomisers are used in pottery ovens dry steam at an average pressure of 20 lbs. per square

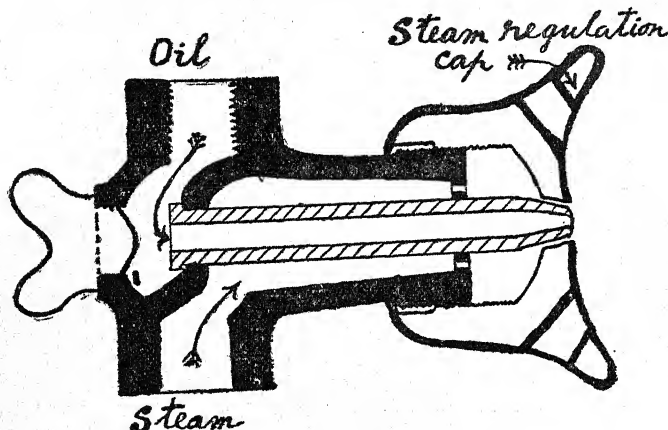


Fig. 29 Wade burner.

inch is used. The consumption of steam is generally taken to be 1.35 lbs. per pound of oil.

Advantages and disadvantages.

Advantages :—

(a) Steam heats up the oil on its passage to the burner and gives better atomisation.

(b) It cools the combustion chambers and saves the refractories from melting.

(c) It carries heat from the combustion chamber in the form of water gas and utilises it inside the kiln.

(d) Most potteries have boilers, and the waste steam can be utilised.

Disadvantages :—

(a) Steam does not support combustion. Hence secondary air has to be admitted without having any control over it.

(b) Steam carries away more heat through the stack, as water vapour has a thermal capacity nearly double that of air or other gaseous products of combustion.

(c) For low temperature firing, the use of steam produces excessive carbonisation.

(d) Steam condenses in the cooler parts of the kiln which is not desirable for its detrimental effects.

Gaseous Fuel.

Natural gas. Enormous quantity of natural gas is obtained from the oil producing regions of America notably from Pennsylvania. The quantity of gas available in winter is much less than that in summer. The composition of these gases not only vary in different localities but also from the same boring at different periods. The principal constituent is Methane (CH_4) which may range up to 90 per. cent.

Average composition of natural gas from Pittsburg Pa.

Methane CH_4	...	83.0 per cent.
Ethane C_2H_6	...	12.0 „
Hydrogen	...	4.5 „
Nitrogen etc.	...	0.5 „

100.0

These gases are largely used in the brick yards of America. As these gases can not be used with regenerators, because the hydrocarbons decompose at higher temperature with deposition of free carbon, their use in high temperature furnaces is limited. These gases are some times compressed whereby the higher boiling members are liquified and sold as liquid fuel.

Coal gas is produced by the destructive distillation of gas coal i. e. long flamed Bituminous coal, in special refractory retorts. The by-products are—coke, gas carbon, tar and ammonia. One ton of good coal yields :—

- (a) Coal gas—10,000 to 12,000 cu. ft. or 18 per cent.
- (b) Tar—14 gallons 6 „
- (c) Ammonia liquor 8 „
- (d) Coke 68 „

The average composition of coal gas.

In small bulk.

Hydrogen	44.8 per cent.
Methane	34.5 „
Hydrocarbons (unsaturated)	4.5 „

Carbon monoxide	...	7.8	„
Carbon dioxide	0.2	„
Nitrogen, oxygen etc,	...	8.2	„

100.0

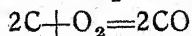
The average calorific value of coal gas is near about 500 B. T. U per cubic foot.

Coke oven gas is obtained as a by-product in the manufacture of coke for the metallurgical purposes. The composition is very much similar to that of coal gas except that the former gas contains more N and CO formed by the action of air on the red hot coke.

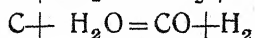
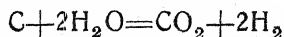
Hydrogen	47.7 per cent.
Methane	26.2 „
Ethylene etc.	3.0 „
Carbon Monoxide	9.0 „
Carbon dioxide	0.5 „
Nitrogen	13.6 „

The heating value of coke oven gas averages about 450 B. T. U. per cubic foot but this useful fuel is not as a rule available for general industrial furnances because it is made in coking plants connected to steel works where all gas produced in the coking plant is used up. One short ton of good bituminous coal produces from 6300-6400 cubic feet of surplus gas.

Producer gas. This is made by the incomplete combustion of solid carbon by the joint reactions of air and steam. When air is used alone the product is only CO mixed with inert N₂ and it is known as *air gas*.



When steam is used alone in decomposing the carbon the products are CO and H₂ which is known as *water gas*.



(900°)

Since water gas requires large amount of heat for breaking up the steam, common producer gas is made by the combined actions of air and steam. Variation in the air-steam ratio produces variation in the composition of the gas.

In order to understand the reactions going on inside a gas producer, let us divide the fuel bed into four zones:—The ash, the combustion zone, the decomposition zone and the distillation zone.

The air and steam first enter the *ash zone* through the iron bars, keep them cool and prevent the ash to fuse into hard clinkers.

The hot air and steam then enters the *combustion zone* where the carbon is converted into CO generating intense heat which keeps the superimposed layer of coal at bright red heat. Each pound of carbon being converted into CO₂ generate 14,647 B. T. U.

The hot gases now passing through the layer of incandescent carbon, or the *decomposition zone*, break down into CO and H₂. Since these decompositions of steam and CO₂ will absorb a large amount of heat, it is evident that only limited amount of steam should be admitted and the fuel bed should be kept at a high temperature.

When the gas is made from coal, the volatile matter in the coal will distil over mostly from the top of the fuel layer or the *distillation zone* and enrich the final gas with various hydrocarbons. If the gas is made

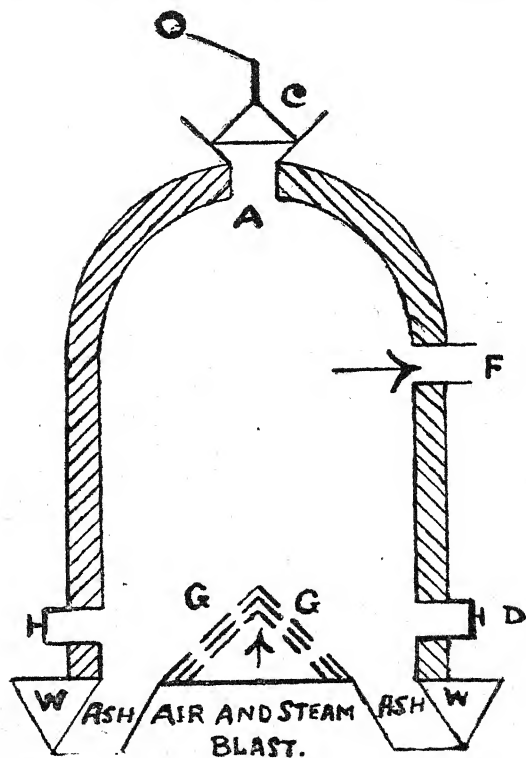


Fig. 30 A gas producer.

from coke or anthracite, there will be practically no hydrocarbon in the producer gas. If the fuel bed is shallow and the amount of steam is low, the producer gets hot when much of the hydrocarbons break up

into H_2 and soot, the solid carbon is also partly converted into CO_2 . The result is a poor hot gas with much CO_2 and H_2 and little CO . The soot clogs the channels of the producer.

But at low temperature CO begins to break down into CO_2 and free carbon, and this action is maximum around $500^\circ C$ and practically eliminated at $1000^\circ C$. In order to regulate between these two troubles a temperature around $600^\circ C$ is advisable inside the producer for average bituminous coal although at this temperature we get soot from the cracking of CO which is less in volume than the soot from the hydrocarbons when the fuel bed gets hot.

This adjustment of temperature of the fuel bed is regulated by the proper admission of steam and air.

In order to decompose 18 lbs of steam into H_2 according to the equation: $-C + H_2O = CO + H$, we require about 124,200 B. T.U. but at the same time we get 53,400 B. T. U. from the conversion of C into CO . Hence we find that to decompose each pound of steam we have to spend 3933 B. T. U. This heat has to be maintained from the oxidation of C to CO or CO_2 .

In practice maximum CO and minimum CO_2 are aimed at. This is gained by removing the CO formed as quickly as possible in order to retard the back action $2CO + O_2 = 2CO_2$. In order to keep up the speed of the removal the fuel bed should be as open as practicable. Bituminous coals have a tendency to swell and form a compact mass which shut up the flow of air and gas.

To remove this difficulty open sandy coal or coke are often mixed with the gas coals. The volatile hydrocarbons of the latter enrich the producer gas.

The gas coming directly from the producer is known as *raw producer gas* and is generally burnt without any cleaning of the gas, in furnaces connected directly with the producer. In this case the sensible heat in the gas, i.e. the heat due to the temperature of the gas above the atmospheric temperature, is utilised. When the raw producer gas is cooled and cleaned of its tarry vapour, it is known as *clean producer gas*. This gas can be stored in gas holders or carried to a distance in iron pipes without clogging them. The thermal values of producer gases are rather low. Heating value of raw gas varies from 125 to 160 B. T. U. while that of clean gas averages at 120 B. T. U. per cu. ft.

Composition of producer gases.

(with Air-steam blast.)

Temperature °C	CO ₂	CO	H ₂	CH ₄	N ₂
440	5.5	26.8	14.6	3.4	49.7
810	6.0	28.3	20.7	4.8	40.2
925	3.0	32.7	17.9	1.2	45.2

Oil Gas. This is prepared by the destructive distillation of mineral oil in special cast iron or fire clay retorts. This gas possesses high illumination and heating power. The great advantage of this gas over coal gas is its power of retaining a large proportion of its luminosity when compressed. Coal gas deposits nearly whole of its liquid hydrocarbons when stored under pressure.

Blast furnace gas is the by-product in the extraction of pig iron. The composition of the gas differs according as coke or coal used.

Composition	With coke fuel.	Hard coal fuel.
CO	27-30	27-30
CO ₂	9-12	8-10
H ₂	1-2.5	4.5-5
CH ₄	—	2.5-4.0
N ₂	57-60	55-58

This gas has very poor calorific value but when mixed with coke oven gas it can serve as very good fuel.

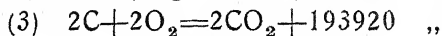
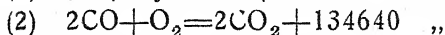
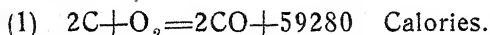
Calorific value of different gaseous fuels.

(B. T. U. per cubic foot.)

Coal gas	450-500
Coke oven gas.	400-500
Producer gas	125-175
Blast furnace gas	95-105

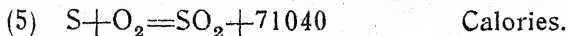
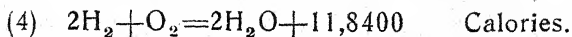
Combustion

Combustion is a process of rapid oxidation of fuels with the development of heat. When any element burns or enters into combination with oxygen, a definite amount of heat is liberated and this fact furnishes us the means of ascertaining the amount of heat produced by a given fuel. Thus when C burns to form CO_2 it generates the same amount of heat, no matter whether it burns in one stage or in two stages.



From the equation (3) we find that 1 kilogram of C burning to CO_2 directly, produces 8080 Calories. If we add the equations (1) and (2) we also find that the same amount of heat is produced when 1 kilo of C burns to CO_2 in two stages.

Similarly the heat generated by 1 kilo of H_2 and S on burning to steam and SO_2 are given by the following equations :—



In other words one kilo of hydrogen produce on conversion to steam 29600 Calories and one kilo of sulphur generate 2220 Calories when converted to SO_2 .

Before the fuel and oxygen can combine together chemically, they must be heated to a suitable temperature which varies with different fuels. This particular temperature is known as the *Ignition temperature* for the respective fuel.

O. Dammer gives the following ignition temperatures.

Peat.....225°C Coal.....326°C

Pine wood...295°C Charcoal...400-800°C.

Dixon and Coward give the following figures for the ignition temperatures of gases.

Hydrogen 580-590°C

CO 644-654 „

CH_4 (Methane) ... 650-750 „

C_2H_6 (Ethane)... ... 520-630 „

C_2H_2 (Acetylene) ... 406-440 „

C_2H_4 (Ethylene) ... 542-547 „

When a fuel like coke burns inside a furnace, sufficient quantity of air has to be provided through the grate bars for proper combustion. This air which has to pass through the fuel bed and chiefly used up in oxidising the C is known as *Primary Air*. When the fuel consists of coal or such other materials which yield volatile combustible gases, a sufficient quantity of hot air has to be admitted for their complete oxidation.

This air which is introduced at the front of the furnace is termed as *Secondary Air* and is generally preheated by passing it through special flues of the furnace or through a recuperating or regenerating system. The function of these systems is to preheat the secondary air by utilising the heat of the products of combustion which would be wasted otherwise. If this secondary air is not preheated the combustible gases 'crack' or break down forming free C or soot, which does not combine with oxygen easily but pass off as smoke, through the chimney.

From the equation (3) given before we find that 24 Kg of carbon require 64 Kg of oxygen for complete combustion to CO_2 . Now air contains only 23 per cent of oxygen by weight so that by simple calculation we find,

1 Kg of Carbon	requires 11.6 Kg of air.	Similarly
1 Kg of Hydrogen	requires 34.8	„ and
1 Kg of Sulphur	„ 4.3	„

Taking the weight of a cubic meter of dry air to be 1.293 Kg we get—

1 Kg of Carbon	requires 8.97 Cu. meter air.
1 Kg of Hydrogen	„ 26.91 „
1 Kg of Sulphur	„ 3.37 „

But in actual practice, the amount of air required is at least 50 per cent more than the theoretical value as a large amount of it passes out through the chimney without helping *in the combustion*.

Gross and net calorific values.

Calorific value of a fuel is the amount of heat generated by unit amount of that fuel. There are generally two main units used. The Calori (big) is the heat required to raise one kilo of water through 1°C .

The British Thermal Unit (B.T.U) is the amount of heat required to raise one pound of water through 1°F .

$$1 \text{ Calori (big)} = 3.96 \text{ B. T. U.}$$

$$1 \text{ B. T. U.} = 0.25 \text{ Calorie.}$$

When a fuel contains H_2 , it burns to form H_2O , which may remain either as steam or condense to water. Water gives up the latent heat as well as the heat liberated on cooling but steam carries away all these heats. The *gross calorific value* is the greater amount of heat theoretically available from a fuel when the H_2O formed is supposed to condense to water.

The *net* calorific value is the theoretical amount of heat obtained from a fuel after deducting the amount of heat carried away by the steam formed.

Calorific value of Coals.

This calculation is based on the assumption made by Dulong that the total amount of heat given out on burning a fuel is equal to the sum of the amounts of heat produced on combustion from its separate elements. The whole of the oxygen present is considered to be already combined with sufficient hydrogen present in

the fuel, to form water. The remaining hydrogen free to burn and produce heat is called *disposable hydrogen*. The following data are employed in the calculation.

1 Kg of C in burning to CO_2 produce 8,100 Calories.

1 Kg of H in burning to H_2O produce 29,000 Calories.

1 Kg of S in burning to SO_2 produce 2,200 Calories.

Heat of vaporising 1 Kg of H_2O at $100^\circ\text{C}=632$ Calories.

The quantity of heat obtained from 1 Kg of coal, is usually calculated from the following formula.

$$\text{Ht (Calories)} = 81C + 290 \left(H - \frac{O}{8} \right) + 22S - 6W.$$

Where,

$H - \frac{O}{8}$ = the disposable hydrogen and W, C, H, O, S

are the percentages of moisture, carbon, hydrogen, oxygen and sulphur respectively.

Problems. (1) Calculate the calorific value of a coal having the following ultimate analysis.

C = 81.2 p. c. H = 5.2, p. c. O = 6.4 p. c.

S = 0.9 p. c. H_2O = 2.1 p. c. Ash 2.2 p. c.

$$\begin{aligned} \text{Ans. Ht} &= (81 \times 81.2) + 290 \left(5.2 - \frac{6.4}{8} \right) + (22 \times 0.9) - 12.6. \\ &= 7873 - 12.6 \text{ or } 7860.4 \text{ Calories.} \end{aligned}$$

(2). Calculate the volume of air required theoretically for the combustion of one kilogram of coal having the above composition.

We have already considered the volume of air required for the theoretical combustion of one kilogram of carbon, hydrogen and sulphur. Using those values we get,

0.812 Kg of C require (8.97×0.812) cubic metres of air.

0.009 Kg of S require (3.37×0.009) " " " "

$(0.05 - \frac{0.64}{8})$ Kg of H require (26.91×0.044) " " "

or $7.283 + 0.030 + 1.184 = 8.497$ Cu. metres.

In the case of gaseous fuels the calorific value is not calculated from the elementary constituents but from the sum of the calorific values of the constituent gases themselves.

The actual determination of calorific values of fuels are made in special calorimeters by burning a certain amount of the fuel either with solid oxidising agents e.g. mixture of nitrate and chlorate of potassium (Lewis-Thompson method), sodium peroxide Na_2O_2 (Parr and Wild method), or with oxygen under ordinary pressure (Favre and Silbermann, Fischer etc. method) or with O_2 at high pressure (Berthelot-Mahler Bomb Calorimeter method).

The calorific intensity of a fuel is the rise of temperature from burning unit weight of the fuel in oxygen under theoretical conditions. The temperature attained depends not only on the heat liberated by the fuel but also on several other factors, such as, the weight of the products of combustion, the specific heat of the gases, the amount of radiation, and excess air

employed. It is therefore not possible to calculate the actual temperature attainable under practical conditions but for theoretical considerations we may assume the following calculations :—

The analysis of a sample of coal gives :—

C=72.45, H₂=4.28, O₂=15.36, H₂O=4.00 and Ash=3.91 per cent. Find its calorific intensity.

$$\text{The calorific value} = (81 \times 72.45) + 290(4.28 - \frac{15.36}{8}) - 6 \times 4$$

$$\text{Or } 5868.45 + (290 \times 2.36) - 24 = 6552.85 - 24. \\ = 6528.85 \text{ Calories.}$$

$$\text{And for 100 Kg. of coal} \quad = 652885 \text{ Calories.}$$

For the theoretical combustion of 100 Kg of this we require :—

$$\text{For C} \quad 72.45 \times 11.6 = 840.42 \text{ Kg of air.}$$

$$\text{For H}_2 \quad 2.36 \times 34.8 = 82.12 \quad ,, \quad ,,$$

$$\text{Total} = 922.54 \quad ,, \quad ,,$$

The products of combustions are :—

$$\text{CO}_2 = \frac{72.45 \times 44}{12} = 265.65 \text{ Kg.}$$

$$\text{H}_2\text{O} = (4.28 \times 9) + 4 = 42.52 \text{ Kg.}$$

$$\text{N}_2 = \frac{922.54 \times 77}{100} = 710.35 \text{ Kg.}$$

Now taking the specific heat of these gases as $\text{CO}_2 = 0.2169$, $\text{H}_2\text{O} = 0.48$ and $\text{N}_2 = 0.2938$, the heat required for raising these products of combustion through 1°C is :—

$$(265.65 \times 0.2169) + (42.52 \times 0.48) + (710.35 \times 0.2938) \\ = 57.619 + 20.409 + 208.618 = 286.646 \text{ Calos}$$

Hence the calorific intensity for 100 Kg. of coal

$$= \frac{552885}{286.646} \text{ or } 2377^\circ\text{C}$$

When there is excess air the temperature would be :—

$$\frac{652885}{(\text{excess air} \times 0.2375) + 286.646} \text{ } ^\circ\text{C where the} \\ \text{sp ht of air} = 0.2375.$$

If the air is preheated then the temperature = $T + \text{Temperature of air}$.

Kilns and Furnaces.

Kilns for ceramic purpose are quite different from other high temperature furnaces as the conditions for burning ceramic articles are quite different. The ceramic materials have in general very low heat conductivity so that the high temperature required for their burning must be raised very slowly. The cooling is also more or less a slow process and the heat radiated from the cooling articles can be utilised as is often done from the chamber or tunnel type kilns.

Each ceramic kiln can be divided into three parts :—

(a) The fire places or the *furnaces*, (b) the *chamber*, and (c) the chimney or the *stack*.

The fuel is actually burnt or gassified in the fire places and the heat or the combustible gases then flow into the chamber where the articles are kept for baking. Here the combustible gases burn imparting

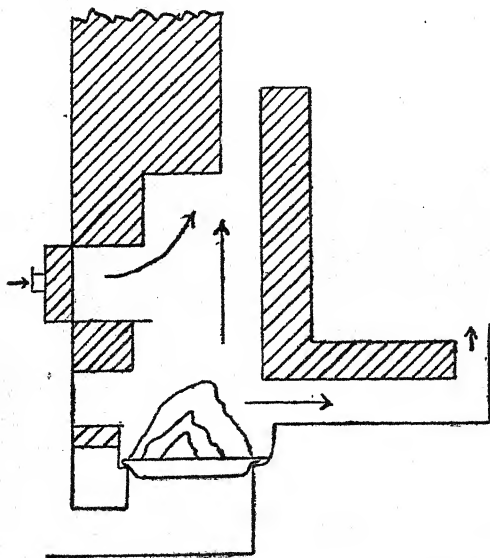


Fig. 31. Flat-grate fire mouth for earthen ware Kilns.

the heat to the articles and then flow out through the flues and the chimney; the latter creating the necessary draught.

The design of the fire places for pottery kilns differ with the nature of fuel used and the temperature to be attained.

For burning wood, grate bars are not necessary. There is generally one fire mouth for kilns using wood, as in burning roofing tiles and terra cotta ware. Glazed pottery of Chunar type are also fired in this type of kiln.

For burning coal, all fire mouths are provided with iron grate bars. In earthen ware kilns the bars are

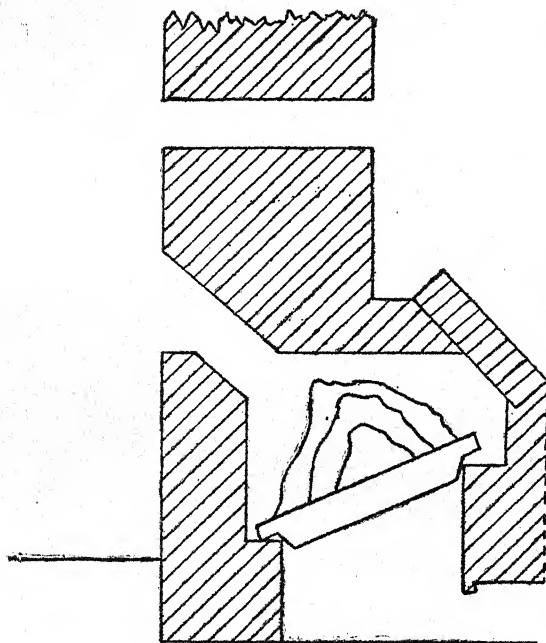


Fig. 32 Inclined grate fire mouth for porcelain kilns.

kept flat and charging of coal is done through doors, near the grate bars, Fig 31. The door is closed after each charging. For admitting excess air when necessary there is another inlet above the charging door. The admission of air through this inlet can be regulated.

In these fire mouths the coal burns more or less completely and the hot products of combustion enter the chamber both from the sides and from below the floor of the kiln.

In porcelain kilns the grate bars are often placed at an inclined position as these fire mouths generally serve as semi-gasproducers, Fig 32. For this reason

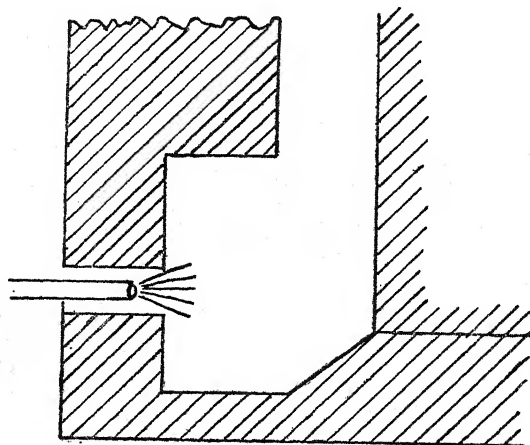


Fig. 33. Fire chamber for oil fuel.

the fuel bed is made deep and the charging is done from the top of the fire mouths. There is no arrangement for the admission of the secondary air through these fire-mouths but separate arrangements are made for preheating this air before it enters into the chamber generally below the crown of the kiln. This preheating is done by utilising the waste heat of the kiln itself.

When oil is used as fuel in pottery kilns, specially designed fire chambers are required. These chambers must have sufficient space to completely burn the atomised oil so that only hot flame and the products of combustion enter into the kiln chamber. Since oil burning produces intense local heat, these fire chambers should be provided with high class refractory lining. In some cases as shown in fig 34 the burner is placed

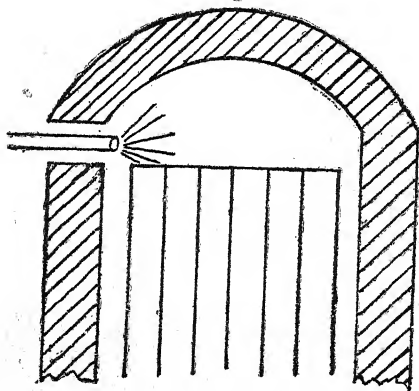


Fig. 34. Oil firing below the crown.

near the crown of the kiln where sufficient space is available below the arch. The hot flames then pass down the chamber round the goods placed in it.

For using natural or artificial fuel gases in ceramic kilns and furnaces specially designed gas burners are used to control the proportions of gas and air for complete combustion, Fig. 35.

The consumption of bituminous coal in pottery furnaces varies from 8-12 lbs. per hour per sq. foot.

of flat grate area. The grate area should not be longer than four feet and wider than three feet in order that they can be cleaned properly without much lowering the temperature of the furnace. The grate bars are square in section with 4 c. m. side and they are placed at equal distance of 4 c. m. from each other. With this distance least quantity of slag is formed and the fall of unburnt coal is within 3 per cent. According to

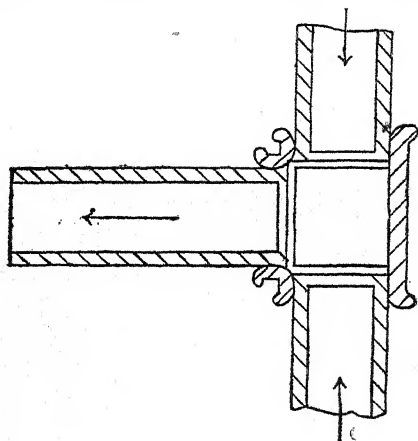


Fig. 35. A gas burner for pottery kilns.

Greaves Walker the relation between the grate area and the floor area of the chamber of a kiln varies between 1:4 and 1:8. For burning of fire bricks the ratio should approach the upper limit i.e. 1:4. For best result in salt glazing the limits should be confined between 1:6 and 1:8. Increasing the grate area will give greater burning speed. For burning high temperature porcelain wares Continental furnaces have a ratio

between 1 : 3·5 to 1 : 5. In the common pottery muffles the floor area of the muffle chamber is generally four times the grate area of the furnaces.

Plenty of space is necessary between the grate bars and the top arch. A low fire box confines the heat locally and heats up the walls which are easily damaged.

The bag walls should be high and round in shape. A high bag protects the ware from flashing and throws the heat more to the centre of the kiln. A semi-circular bag wall gives longer life.

The chamber is the place where the wares are kept for baking. These chambers are either rectangular or round in shape. Particular care has to be taken in setting the wares inside the chamber so that internal channels are provided for the proper flow of hot gases which impart the heat to the wares. The problems inside the chamber are to transfer as much heat as possible from the hot gases to the wares, and to distribute the heat evenly throughout the chamber so that all parts of the chamber get equally hot. It has also to be seen that the wares are protected from sudden changes of temperature, the gaseous products of combustion and the solid particles of the fuel and ash carried into the chamber by the current of gases.

The gases pass through the kiln either by a pressure created at the fire places or by a suction caused at the exit end by a fan or chimney. In the former case there is chance of hot gasses leaking out from the chamber where as in the latter case cold air gets into

the chamber through small cracks or openings on the walls, cooling them to a certain extent. The walls and crowns of kilns working under a positive pressure, are considerably hotter than those where the kilns are working under a negative pressure, so that in the former case the refractories are subjected to more severe conditions. Kilns working with oil or gas fuel have a positive pressure inside and generally do not require a chimney to create a draught.

Walls and Crown. The wall should be sufficiently thick to stand the strain and prevent excessive radiation but it should be thin enough to conform a good fire box design. A thick wall concentrates the heat in the fire boxes, thereby entailing heat loss in the walls and high repair charges through frequent burning out of the fire box arches.

Considered from all angles, thin straight walls are the best if they can be insulated, as in this case the fire box is thrown inside the chamber and the fuel does not waste considerably of its energy in heating up and burning out the walls. The setting space lost by projecting the boxes into the chamber, while a considerable item, cannot be compared with the saving of time, fuel and repairs, during the life of a good kiln. If an un-insulated wall is built it must be as thick as possible and still be compatible with good fire box design.

Walls of rectangular kilns are built thicker than those of round ones as the bands (iron) on round kilns are much more efficient than those on rectangular kilns. For kilns firing up to 1100°C the fire brick lining

need not be more than $4\frac{1}{2}$ " thick. For higher temperatures 9" linings should be used. In a round kiln it is not necessary to tie the fire brick lining to the common brick wall as in this case the lining may expand and contract without reference to the main wall and it is much easier to repair. In a rectangular kiln it is always necessary to tie the fire bricks to the main wall.

If the round kiln is not insulated the wall should not be over forty inches thick and for rectangular kiln it should not exceed 48 inches.

When $4\frac{1}{2}$ inches insulating lining is used the round kiln wall may be 24 inches (F. B. 4.5", I. B. 4.5", C. B. 15") and the rectangular kiln walls 36 inches. It even pays to make porous common bricks for the exterior of the wall as they are better insulators than hard ones.

For a round crown the height of the crown from the shoulder should be $\frac{1}{4}$ the diameter of the kiln. For a rectangular kiln this distance is $\frac{1}{3}$ of the inside width.

A kiln with a high crown consumes more fuel, takes longer to burn and gives poorer bottoms than one with a low crown. If the crown is too low the top ware is likely to be over burned.

The crown should be supported on the main wall and not on the inner fire-brick lining. This enables repairs of the crown or the wall lining independent of each other.

Modern kilns are generally insulated with special insulating bricks which are made from naturally occurring infusorial or diatomaceous earths rich in silica. When properly burnt they are highly refractory and low

in heat conducting power due to their having innumerable microscopic pores.

The insulation not only reduces the loss of heat through radiation by 16-20 per cent but it also improves the quality of the fired articles and reduces the time of burning.

High temperature insulating brick properties.

Properties	Fire brick.	A	B	Remarks
Weight. lb.	8	3.7	2.5	A = Artificial brick made with clay & organic matter.
Shrinkage at 1400°C.	0.0	5.6	3.9	
Thermal conductivity at 1100°C.	0.0040	0.0017	0.0011	B = made from infusorial earth with small pores.
Resistance to temp. changes.	good.	good.	poor.	

Analysis of Infusorial Earths.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaCO ₃	H ₂ O	Loss.
Oberholl-Germany	87.9	0.1	0.7	0.7	8.4	2.3
California U. S. A.	85.3	5.4	1.1	1.1	5.6	...

One inch of Kieselguhar of California has insulating quality equal to twelve inches of common brick. A four inch lining of insulating brick in a furnace wall which is under constant heat, will prevent 50 to 75 per cent of the radition.

Large air spaces are not efficient insulators at very high temperatures as are found in furnaces. The pores must be infinitesimal in size so that air circulation may not be set up when there is a difference of temperature between the two sides.

Flues and stack. The gaseous products of combustion of the fuel used in the furnaces pass out of the chamber through several flues or channels into the chimney or stack. The dimensions and number of these flues should be so adjusted that the gases pass out easily without creating any trouble inside the chamber. In order to find out the general formula for determining the cross section of flues we may consider as follows,

General formula for the cross section :

Let M = daily consumption of coal.

So the consumption per second $\frac{M}{86400}$ Kg.

Let A = Cu meter of gas-product per Kg. of coal.

Hence the volume of gas evolved per second :—

$$= \frac{AM}{86400} \text{ Cu. Meter.}$$

If T = the temperature of the gas, the volume of the gas

$$= AM \frac{\left(1 + \frac{T}{273}\right)}{86400} \text{ Cu: Meter per sec.}$$

Now when V = the velocity of the gas in the flue we get

$$\text{Cross sec.} = AM \frac{\left(1 + \frac{T}{273}\right)}{86400 \times V} \text{ Sq. meter.}$$

We have already found out in a previous example that 100 Kg. of coal of the given composition produce 1018.52 Kg. of the following gaseous products of combustion.

$\text{CO}_2 = 265.65$; $\text{H}_2\text{O} = 42.52$ and $\text{N}_2 = 710.35$ Kg,

Now taking the weight of one Cu meter of these gases to be; $\text{CO}_2 = 1.9659$, $\text{H}_2\text{O} = 0.8042$ and $\text{N}_2 = 1.2510$ Kg.

We find that 100 Kg. of the coal produces—

$\text{CO}_2 \dots 135.5$	Cu.	Meter
$\text{H}_2\text{O} \dots 53.1$	„	„
$\text{N}_2 \dots 568.0$	„	„
<hr/>		
Total. 756.6	Cu. meter.	

Thus we find that each kilogram of coal produces theoretically 7.56 Cu meter of products of combustion but in actual practice 30-50 per cent excess air is required. The average velocity of gases in the channels and flues of pottery kilns is near about 8-10 ft. per second, and the calculation for the cross section can be based on this rate.

The stack or chimney provides the suction or pull to create a natural draught inside the kiln. This pull of a chimney is due to the difference in weights of equal volumes of atmospheric cold air and the hot kiln gases. The draught should be sufficient to overcome all the resistances through which the gases have to pass in their passage through the kiln and flues and to give the flowing gases a sufficient speed in the chimney not to be too much affected by the outside wind. In order to solve these problems effectively the height of the chimney should be calculated from the following considerations.

Stack Calculations.

Total Head of the chimney. The suction or pull which a chimney can produce is simply due to the ascensive force of the hot gases, and this is measured by the difference in weights between the column of hot gases inside the chimney and an equal volume of air at the outside temperature. When this force is expressed in terms of cold air at 0°C , it is known as the total head of the chimney.

Thus if, H and S are the height and cross section of the stack respectively and if Q and t are the temperatures of the atmosphere and the hot gases, while d , d_1 are the relative densities of the air and gases respectively at N. T. P, then total ascensive force would be :—

$$(1) \dots\dots H.S. \left(\frac{d}{1+LQ} - \frac{d_1}{1+Lt} \right) \text{Kilos or pounds.}$$

$$(2) \dots\dots H \left\{ \frac{d}{1+LQ} - \frac{d_1}{1+Lt} \right\} \frac{\text{Kilos}}{\text{Sq.M}} \text{ or } \frac{\text{Pounds}}{\text{Sq. ft.}}$$

$$(3) \dots\dots H \left\{ \frac{d}{1+LQ} - \frac{d_1}{1+Lt} \right\} \frac{\text{Meter of air at } 0^\circ\text{C.}}{d} \text{ or } \text{feet of air at } 0^\circ\text{C.}$$

Illustration :—

A chimney is 50 meters high and 3 meters square inside. The hot gases flowing through it have an average temperature of 300°C . The outside temperature is 30°C . Find out the total Head of the Chimney.

(Take $d=d_1=1.3$ Kilos per Cubic meter).

The total force in Kg

$$= 50 \times 9 \left(\frac{1.3}{1+0.00366 \times 30} - \frac{1.3}{1+0.00366 \times 300} \right)$$

$$= 450 \left(\frac{1.3}{1.1098} - \frac{1.3}{2.098} \right) = 248.22 \text{ Kg.}$$

$$\text{Or } \frac{248.22}{9} = 27.58 \text{ Kg per Sq. meter.}$$

Now since the weight of a cubic meter of air at N.T.P. is 1.3 Kg, the total pull of the chimney is therefore equivalent to—

$$\frac{27.58}{1.3} \text{ or } 21.21 \text{ meter of air at } 0^\circ\text{C.}$$

or 21.21×3.28 or 69.56 feet of air at 0°C .

Since water is about 772 times heavier than air, the above heads in terms water gauge would be :—

$$\frac{21.21}{772} \text{ or } 0.027 \text{ meter of water gauge.}$$

or

$$\frac{69.56}{772} \text{ or } 0.088 \text{ feet of water gauge.}$$

Velocity Head of issuing gases :

The velocity (V) acquired by a fluid is the same as the height (h) which a falling body must fall in order to acquire the same velocity, i. e.

$$h = \frac{V^2}{2g}, \quad g = 9.8 \text{ meters or } 32.2 \text{ feet per sec.}$$

Thus if we know or assume the velocity of the hot gases issuing from the chimney, we can get (h) which is the force expressed in ft. or meter of the gases to move the chimney gases at a fixed velocity.

In general this (h) is expressed in terms of cold air at 0°C and is known as *Velocity Head*. In order to calculate it we must take into account the relative densities of the hot gasses and the cold air which are inversely proportional to their absolute temperatures.

If d_1 = density of gases at 0°C .

d = density of air at ,,

$$\text{Then V.H. (gas at } 0^{\circ}\text{C)} = \frac{h \cdot d_1}{1 + Lt} \text{ or } \frac{V^2}{2g} \left\{ \frac{d_1}{1 + Lt} \right\}$$

$$\text{Similarly V.H. (Air at } 0^{\circ}\text{C)} = \frac{V^2}{2g} \left\{ \frac{d_1}{(1 + Lt) d} \right\}$$

Where t = Temperature of the chimney gases and

L = Coefficient of expansion of gases

$$= \frac{1}{273} \text{ or } 0.00366 \text{ per degree C}$$

$$\text{or } 0.002 \text{ per degree F}$$

Illustration :—

The velocity of the issuing gases from a chimney is five meters per second. The temperature of the gases is 300°C . Calculate the V. H. of the Chimney. The density of air at $0^{\circ}\text{C} = 1$ and that of the gases $= 1.06$.

$$h = \frac{V^2}{2g} \text{ or } \frac{25}{2 \times 9.8} = \frac{25}{19.6}$$

$$\text{V. H. (gas at } 0^{\circ}\text{C)} = \frac{25}{19.6} \times \frac{1.06}{1 + 1.098}$$

$$\text{V. H. (cold air)} = \frac{25}{19.6} \times \frac{1.06}{(2.098) d}$$

$$= 0.64 \text{ meters of air at } 0^{\circ}\text{C},$$

$$\text{or } 2.099 \text{ feet of air at } ,,$$

Friction Head of a Chimney. Friction Head of a chimney is the resistance offered by its sides expressed in terms of cold air. It varies with the nature and roughness of its walls and is expressed as :—

$$\text{F. H.} = \text{Velocity Head} \times \frac{h}{s} k. \quad \text{Where}$$

h is the height of the Chimney,

s is the diameter or side inside,

k is a varying factor.

As determined by Grashof k varies between 0.05 for a smooth interior to 0.12 for a rough one. Lovejoy advocates a value of 0.1 for pottery stacks.

Illustration :—A Chimney is 50 meters high with three meters side. The total velocity head is 0.64 meters of cold air. What is the head lost due to friction in the chimney ?

Taking $k = 0.1$ we get.

$$\text{F. H.} = 0.64 \times \frac{50}{3} \times 0.1$$

or 1.066. meter of Cold Air.

Grate and Kiln Resistance : Air while passing through the grates where coal is burning and the gases while passing through the kiln set up with wares have to overcome the friction resistances offered by them. It is not possible to give any general data for all kilns or even of the same kiln fired under different condi-

tions. But we shall not be far astray if we adopt the boiler data calculated by Prof. Gale, for our periodic kilns. In a test of a boiler, Gale found that the total grate and tube resistances require a stack intensity of 0.4 inch of water. or

$$\frac{0.4 \times 772}{12} = 25.73 \text{ feet of air.}$$

$$\text{or } \frac{0.4 \times 772}{12 \times 3.28} = 7.84 \text{ meter of air.}$$

Stack height: In order to calculate the total height of a chimney set on the kiln or without any extra flue, we may consider as follows :—

The total intensity of pull caused by the chimney = the grate and klin resistance + the velocity head + the friction head.

But when the stack is situated at a distance from the kiln, the length of the connecting flue should also be considered.

Illustration :— It is desired to find out the height of a chimney with three meters side. The hot gases flowing through it has an average temperature of 300°C with a velocity of five meters per second. The outside temperature is 30°C.

Solution :— The total intensity of pull is—

$$H. \left\{ \frac{d}{1+LQ} - \frac{d_1}{1+Lt} \right\}$$

d

Taking $d = d_1 = 1.3$ we get as before :--

Pull = $0.424H$ meter of cold air. Similarly

The Velocity Head = 0.64 meter of air.

Friction Head = $H \times 0.021$ meter of air.

Grate and Kiln resistance = 7.84 .

$\therefore 0.424H = 7.84 + 0.64 + 0.021 H$.

Or $0.403H = 8.48$. $H = 21$ meters.

Special consideration should be given for the construction of high temperature stacks. As a basis for average conditions it is customary to make the inner diameter or the side of a square stack as many inches as the kiln is feet in diameter. The inside lining should be of fire bricks. The inner surface of this lining should be as smooth as possible so that there is least resistance offered to the flow of gases. An air space ($2\frac{1}{2}$ ") should be kept between the inner linings and the outer walls made of well burnt common bricks and there should be connections (headers) between the outer walls and the inner linings to keep them steady. The velocity of gases in factory chimneys varies from 10-20 feet per second.

Modern pottery kilns can be classified under the following heads :—

A. Periodic kilns.

- (1) Open top kilns.
- (2) Crowned kilns. (a) Up draught kilns (b) Down draught kilns (c) Horizontal draught kilns.
- (3) Muffle kilns.

B. Continuous kilns.

- (1) Rectangular kilns.
- (2) Chamber kilns.
- (3) Tunnel kilns.
- (4) Circular kilns.
- (5) Tunnel muffle kilns.

Periodic kilns are used for their low cost of construction and the flexibility of operation. Their disadvantages are—high fuel consumption, unevenness of temperature inside the kilns and the strain on the brick-work due to repeated heating and cooling. For these reasons, the periodic kilns are being gradually displaced by continuous kilns but they will always be used in smaller factories, and for burning large and intricate shapes where the burning schedules are different from ordinary ware.

In continuous kilns the initial cost is higher than that for periodic kilns. Practically the heat loss of these kilns is only by radiation through the walls and the tops, for heat is abstracted from the cooling wares and the combustion gases. Other advantages of continuous kilns can be summed up as follows :—

- (1) The refractories of the kiln structure are not subjected to great strain which minimise the upkeep cost of the kiln.
- (2) The distribution of heat inside the kilns is more or less uniform which produces well burnt uniform ware.

- (3) Due to continuous and regular operation the setting and drawing cost is somewhat minimised.

According to Greaves Walker's calculations the amount of heat actually used by wares in a periodic brick kiln is only 19.55 per cent of the total heat used for burning the ware. He puts the different sources of heat loss in the following proportions.

Heat balance of building Brick kiln burnt to 2000°F.

Heat lost by flue gases	27.33
Heat lost by ashes.....	3.51
Heat lost by radiation and cooling.	49.61
Heat used by the bricks.	19.55
	<hr/>
	100.0

The efficiency of tunnel kilns is as high as 45 per cent or more when compared with the value of 19.5 per cent for periodic kilns. Norton has given the following figures for the consumption of coal for burning one thousand bricks of normal size up to 1270°C.

Round down draught.....	2,200 lbs. of coal.
Rectangular down draught ...	1800 lbs of coal.
Car tunnel kilns.....	700-800 lbs of coal.

The simple types of open top periodic kilns are known as *clamps* and are mainly used for burning common bricks. The clamp consists of a structure of unburnt

bricks and fuel arranged temporarily before each fire. The fuel is placed alternately between the layers of bricks which are so arranged that sufficient air can pass between them to burn the coal and allow the hot gases to circulate between them. The advantages of periodic clamp kilns are, their low cost of construction, large or small structure according to demand, fuel economy, and no storage space required for the bricks.

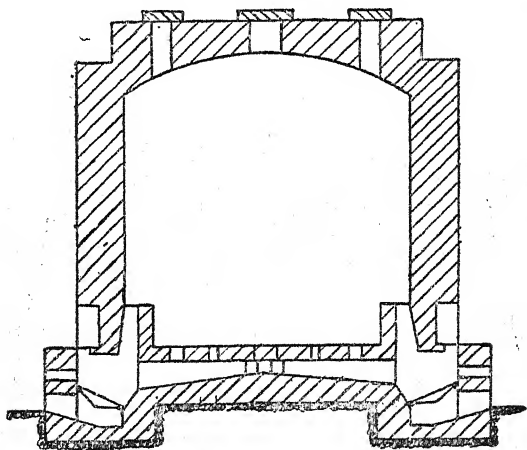


Fig. 36 An up draught kiln.

The disadvantages on the other hand are, excessive loss in broken, overfired, or underfired bricks and no control on the natural elements such as rain, storms etc.

The simplest improvement on this open clamp firing was to surround the wares with brick walls with special bricks previously fired. When this structure is covered with a roof it forms the simplest type of crowned kilns. The articles to be burnt are placed

inside this kiln and fired from outside through specially constructed holes or fire places built on the sides of the walls. Openings are left on the arch of the crown to let out smoke and fire gases. Since the draught inside these simple kilns are upwards passing out through the chimney constructed at the top, they are generally known as up draught kilns.

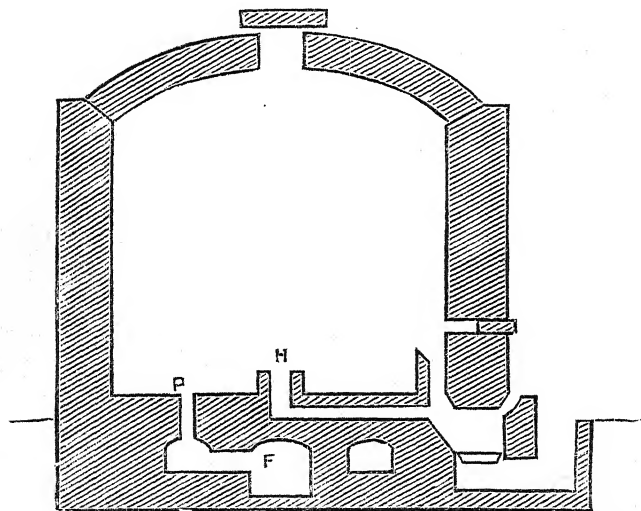


Fig. 37 A down draught kiln.

Periodic kilns with a down draught have either one or two chambers, the one above the other. A single chambered kiln of this type is shown in fig. 37 but the chamber may also be rectangular or square and the chimney or stack built at one side of the kiln. In these kilns, the distribution of heat inside the chamber is

more uniform than in the previous ones and there is less chance of goods being overfired in one part of the kiln and underfired at other parts. These kilns are generally 10 to 15 feet high and the fire places are united by flues beneath the floor which join in one central inlet (H) for the flames.

When the gases and flames have entered the kiln they rise upwards, strike the crown and are reflected by it in a series of parallel streams to the floor of the kiln. If the shape of the crown is properly constructed, the reflected heat would be uniformly distributed over the whole area of the kiln. The gases in passing downwards, circulate among the articles to be heated and then pass out through the openings in the floor (P). All these openings lead to a central well, which communicates by an underground flue (F) with an outside chimney, which usually serves for several kilns. There may be one or more damper on the crown of the kiln to control the heating and hasten the cooling after the burning is finished.

For firing fine earthen ware, a special type of down draught kiln as shown in fig 38 is largely used in England. The fire boxes 9-11 in number throw up the flames through the *bags* or openings around the inner wall of the kiln, and also up a central hole on the floor of the kiln called the *well* which is connected to each fire box by flues, built under the floor. Thus the hot flames and gases from the fire mouths, go straight up, both at the centre and the circumference of the oven till they strike the crown and are diverted downward. The hot

gases are then carried off through the openings in the floor which are connected to the flues built inside the walls of the kiln between the firing boxes, and opening

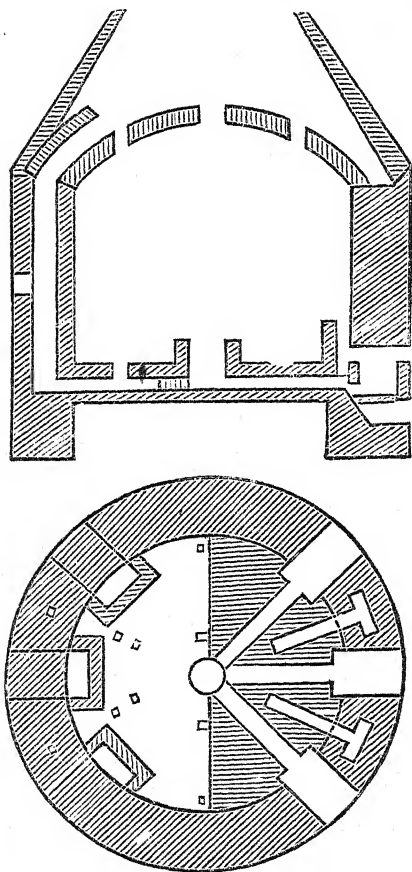


Fig. 38. An English Earthenware oven.

into chimney built above the crown. This system increases the heat efficiency of the oven.

There is a big exit flue at the centre of the crown with a damper, and also one or two small flues with dampers at each quarter of the crown, so that when one part of the oven goes in advance to other parts, the dampers above the advanced part can be opened a little and the temperature inside the whole oven adjusted. These ovens can be used exclusively for up-draught work also with the crown vents open and the wall flues closed. These ovens are generally made 15 to 20 feet high and nearly as much wide. Having equal capacity, ovens with short height are more economical in labour and saggar breakage than high ovens with short width.

The two-chamber kilns are improvements on the single-chamber ones specially for fuel consumption and economy of time. A typical kiln of this type is shown in fig. 39 which is specially made for porcelain firing. The upper chamber which is heated by the hot gases from the lower one is generally used for baking the wares before glazing.

The flames and hot gases from the fire boxes enter into the lower chamber through the bags along the sides of the wall and rise upwards to the crown, from where they are deflected downwards in parallel currents and pass along the sides of the saggars, then through the apertures on the base and again rise up the flues in the walls of the kiln to the second chamber above. From this second chamber the gases go up through the chimney, constructed on the top of the second chamber.

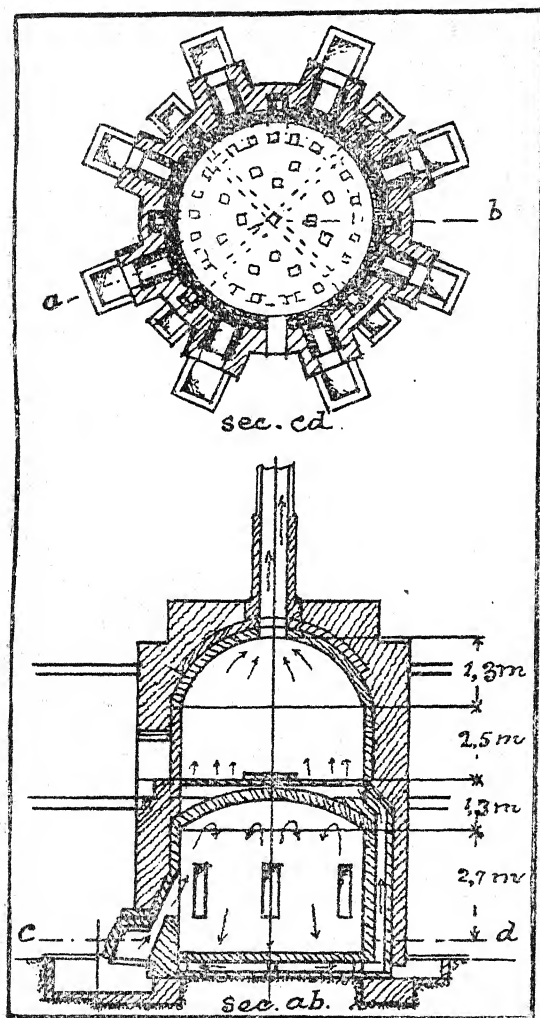


Fig. 39. A double chamber porcelain kiln.

These kilns do not have bag wells projecting inside the chamber to get increased sagger space, but in order to protect the first ring from too severe heating, in some types of kilns like *Sevres porcelain oven*, the ordinary bags are replaced by a high circular wall running round the firing boxes within a few inches of the oven wall, and as high as the shoulder of the oven. This wall gives protection to the wares in the first ring,

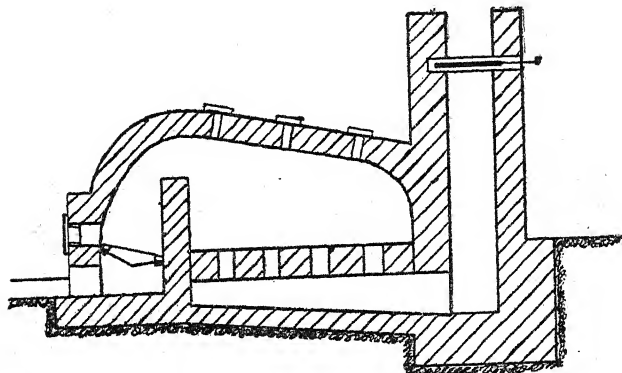


Fig. 40. Cassel horizontal kiln.

and throws all the heated gasses to the top space of the oven under the crown, which becomes the final combustion chamber from where the gasses pass downwards between the saggars.

The horizontal periodic kilns of *Cassel* or *Newcastle* types have generally one fireplace at one end of the kiln and a chimney at the other. The flames travel horizontally along the length of the kiln and pass out through the chimney. If the kiln is short in length, the

distribution of heat is fairly good, whereas in longer kilns, the goods suffer from want of proper distribution of heat. These kilns are specially suited to the production of high temperatures, such as are needed for burning fire bricks, but they are very wasteful in fuel.

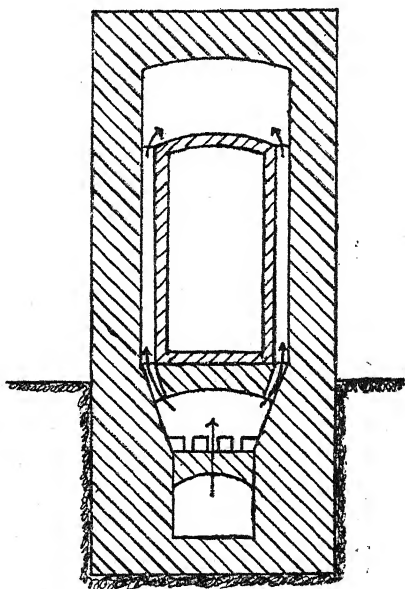


Fig. 41. A muffle kiln.

Muffle kilns are used for burning enamel colours on pottery and for all such wares which must be protected from the direct contact with fuel gases. The periodic or intermittent muffles are rectangular chambers with walls made of refractory materials and heated from outside, so that the inside chamber is only heated

by the radiation and conduction of heat through the walls. It is important therefore, that those walls should be as thin as practicable and the refractory materials must have fairly good heat conductivity. These kilns are constructed in such a manner that the flames and gases circulate in the space between the furnace walls and the muffle box of the kiln and finally collect in a common flue and escape through the chimney.

Continuous kilns.

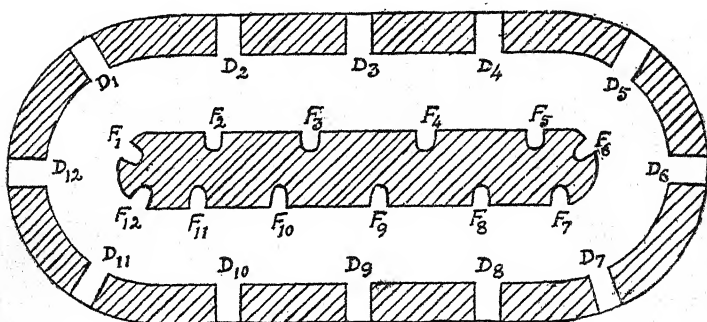


Fig. 42 Plan of Hoffman kiln.

Hoffman kiln is the typical specimen of continuous rectangular kilns. All other kilns of modern construction follow the same principle with some improvements here and there. The working principle of this type of kilns consists in having a rectangular burning chamber with twelve doors D_1 D_2 D_3 etc. for filling, and twelve flues F_1 F_2 F_3 communicating with a main flue which is connected with a central chimney.

These twelve flues are quite independent and can be opened and shut by means of twelve bell dampers. The space between two such consecutive dampers is called a chamber and generally separated by temporary partitions. The fire is started by building temporary fire places in an empty chamber adjacent to the goods to be fired, and by this means the ware is sufficiently heated to ignite the coal thrown through feed holes in the roof of the chambers Fig. 43, and the kiln begins its normal working.

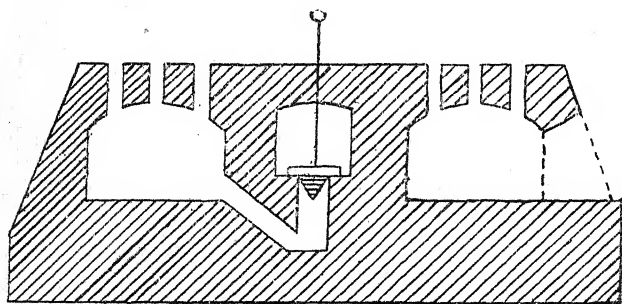


Fig. 43 Hoffman kiln. End view.

The hot gases are made to pass from one chamber to another until they lose their heat and reach a temperature of about 150° to 200°C . It is then useless to carry them through any more chamber, so they are taken to the chimney through the main flue.

Continuous kilns with permanent chambers are more suitable for wares which are delicate in nature and need a very high temperature, because it is not possible to regulate the composition of the atmosphere inside the

kilns where the firegases travel in a horizontal direction as in the case of kilns of Hoffman type. Also the distribution of temperature inside these kilns is not very satisfactory.

For this reason a chamber kiln of *Mendheim* type, especially a gas-fired one, is in general use for firing better class goods at high temperatures. In this type of kilns each chamber communicates with the following one

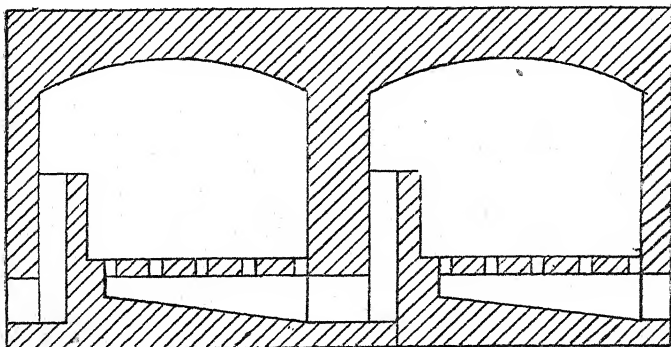


Fig. 44. Mendheim Chamber kiln.

by flues, starting at one corner, going underneath the floor and ending in the next chamber. The gas is led into each chamber through an outside underground flue while the draught is caused by a central chimney.

Tunnel Kilns. The idea of a tunnel kiln for burning pottery ware was conceived not less than 160 years ago but its development on practical lines was done by Otto Bock in Germany about 60 years back only. In this type cars or trucks are made to travel on iron rails

inside a long tunnel 200-350 feet in length, four to twelve feet wide and with a space of about five feet between the car decks and the crown. The cars are covered with a refractory platform upon which the wares are placed. An iron apron attached to each side of the deck and a sand filled trough on both sides of the kiln walls cut off the metal portion of the car and the undertunnel from the hot gases. Fig. 46.

The air supply enters under the cars through the lower passage at the stack end of the tunnel and flows along the length of the tunnel keeping the lower portion

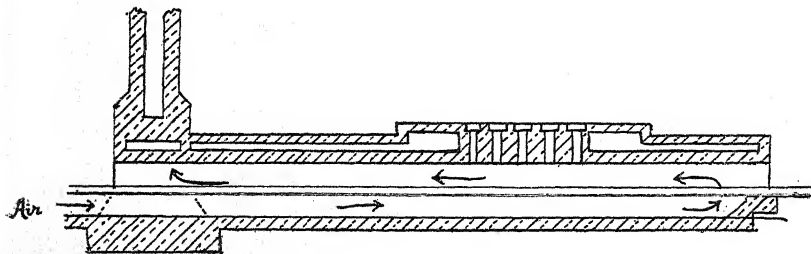


Fig. 45. Sectional view of Bock tunnel Kiln.

of the cars cool. It then enters the main tunnel at the opposite end, thence travelling backwards successively through cooling, combustion and heating up zones, give up its available heat to the incoming wares, before it passes out through the chimney. Fig. 45.

Bock tunnel kilns were originally fired with coal fed through holes in the crown of the firing zone but about five years later the Siemens-Hesse car tunnel kilns appeared with producer gas firing.

When this type of kilns are adapted to a certain class of ware, there are undoubtedly some advantages over the types of kilns, and those may be summarised as follows :—

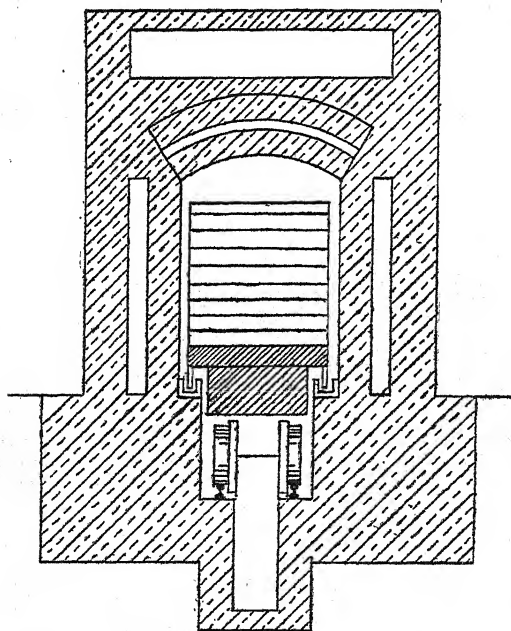


Fig. 46. End view. Bock tunnel Kiln.

- (a) Marked economy in fuel consumption.
- (b) A fixed hot zone reduces the heat absorption loss and also loss due to radiation.
- (c) Less cost in the upkeep of the tunnel. High grade refractories required only for the combustion zone.

- (d) Less breakage of the ware due to easier handling.

Circular Kilns. Circular-kilns are rapidly becoming popular in the European countries and America. In this kiln the shape of the tunnel is circular instead of being straight, otherwise the construction principle is more or less the same. It is claimed that the capital cost of building a circular tunnel is less than that of a straight tunnel kiln and there is no need of shunting the trucks for charging and discharging; the labour cost is also reduced.

Continuous muffle kilns of the *Dressler* type are largely used now-a-days for firing all kinds of pottery wares. This kiln can fire upto a temperature of about 1300°C and require no saggar boxes for placing the goods.

The operation of the *Dressler* tunnel kilns differs materially. The air for combustion enters at the delivery end and passes through the tunnel in contact with the cooling ware up to the combustion zone. In this zone, on each side is a combustion chamber C_1C_2 built of fire clay and carborundum. The gas is delivered into these combustion chambers through a cross duct under the kiln base. The air is drawn into the combustion duct through ports in the furnace bench. The air is heated by the cooling ware before it enters the combustion chambers near the longitudinal centre of the kiln and the combustion gases are drawn along the heating up zone by means of ducts and pipes. Thus the combustion gases do not come

in contact with the ware so that this type of kilns do not require any saggar for protection of the ware from the injurious effects of the combustion gases. The draught is caused either by a stack or a fan and the hot gases are often utilised for other purposes.

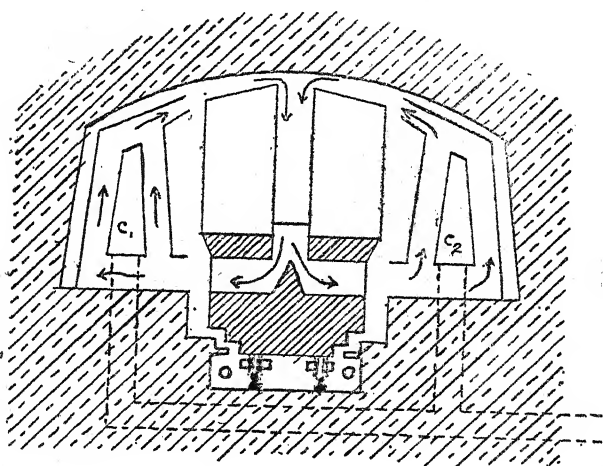


Fig. 47. Dressler tunnel Kiln.

The recent advancement in pottery firing is the employment of electricity. Already a few types of electric kilns have been brought out in the market, and these kilns are successfully firing glost wares and decorations on pottery and porcelain. The advantages of these kilns are :—

- (1) Clean oxidising atmosphere free from any smoke or fume.

- (2) Uniformity of temperature, with the result that all the wares are uniformly treated.
- (3) Economy of labour and simplicity of control in the operation.
- (4) Low repairing cost.
- (5) Economy of time.

The only disadvantage is the high cost of electricity.

Comparative efficiency of different kilns.

Periodic down draught kiln	...	15 to 19 per cent.
Hoffman Rectangular kiln	...	21 to 23 „
Tunnel kilns gas fired	...	41 to 43 „
Dressler kiln gas fired	...	47 to 49 „

CHAPTER XI.

PYROMETRY.

In order to ascertain the temperatures inside the ovens, various devices are used from time to time. The simplest but one requiring the most skilful experience is the estimation by eyes according to the changes of colours of the hot wares or the sides of the ovens, due to the rise of temperature: The information in the following table gives an approximate relation between the changing colours inside a hot oven and the corresponding temperatures.

Just visible Red	500°C
Dark Red	700°C
Just Cherry Red	800°C
Bright Red	1000°C
Bright Orange	1200°C
Bright White	1300°C
Dull White	1400°C
Shining White	1500°C

The tint inside the oven should be judged only when the flames are clear, and free from any hydrocarbon. The observer should stand in a dark place so that his eyes may not be influenced by the varying brightness of the sunlight.

For all pottery industries, where more exact firing is needed, pyroscopes, or pyrometers are used to determine the temperature.

Pyrosopes. These are small devices made of ceramic materials to indicate the temperature inside a pottery kiln by the action of heat on the materials of which the pyrosopes are made. They can be used for once only as they either melt down or contract permanently. There are various types of these pyrosopes placed in the market from time to time. The more important ones are:—Wedgwood's Cylinders, Seger's Cones, Holdcroft's Bars, Buller's Rings, etc.

In the year 1782 Josiah Wedgwood the famous English potter introduced a special form of pyroscope in order to measure the temperature inside a potters

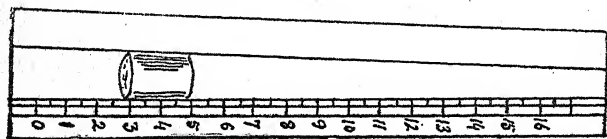


Fig. 48. Wedgwoods Pyroscope.

kiln. The device was so simple but it was very helpful to those early potters for more than a century.

In this device small bits of clay cylinders of a definite composition are placed inside the kiln and withdrawn at different stages of firing. The withdrawn bits are allowed to cool and then their contractions are measured by a specially designed scale which indicates the temperature. This simple method is helpful when the rise of temperature inside the kiln is steadily progressive but during the soaking period of the kiln firing the shrinkage of the bits will not be regular.

A *Seeger Cone* is a device, introduced by Herman Seger of Germnay in 1886 to determine the temperature inside a pottery kiln. These Cones are made of pure ceramic materials such as washed clays, felspar, quartz, marble, ferric oxide etc. These Cones are made in two standard sizes. The ordinary-size Cones are made of three sided pyramids with a height of about $2\frac{1}{4}$ inches and a base of about one fourth the height. The small size is about an inch long with one fourth of an inch base. The small size is mainly used for small experimental furnaces and for testing the refractoriness of fire clays.

When Dr. Seger first introduced his Cones, he numbered his set from Cone No. 1 softening at about 1150°C . These Cones became so useful that the series was extended by Cramer to higher temperatures and later by Hecht to lower temperatures by using boric acid and lead oxide in proper proportions. The result was that there were 64 Cones in the series. In order to avoid disturbing the numbers given by Seger, already in use, Cones softening at temperatures lower than Seger's No. 1 were numbered downwards from 1 by affixing a cypher. Thus Cone 01 softens one Cone below Cone No. 1 and Cone 02, two Cones below No. 1 etc. The whole series runs from Cone 022 softening at about 600°C to Cone 42 softening at about 2000°C . About 1909 it was thought advisable to eliminate lead and iron oxides from the compositions of Cones because of the deliterious effect of reducing atmospheres on these oxides bearing Cones. As a result the old Cones containing

lead and iron oxides were replaced and renamed by putting an 'a' after the cone number. Again the five old Cones from No. 21 to 25 were found to squat so near each other that they were abandoned.

Table for approximate softening temperature of Seger Cones.

Cone No.	Temp. cent.	Cone No.	Temp. cent.	Cone No.	Temp. cent.
022	600	02a	1060	19	1520
021	650	01a	1080	20	1530
020	670	1a	1100	26	1580
019	690	2a	1120	27	1610
018	710	3a	1140	28	1630
017	730	4a	1160	29	1650
016	750	5a	1180	30	1670
015a	790	6a	1200	31	1690
014a	815	7	1230	32	1710
013a	835	8	1250	33	1730
012a	855	9	1280	34	1750
011a	880	10	1300	35	1770
010a	900	11	1320	36	1790
09a	920	12	1350	37	1825
08a	940	13	1380	38	1850
07a	960	14	1410	39	1880
06a	980	15	1435	40	1920
05a	1000	16	1460	41	1960
04a	1020	17	1480	42	2000
03a	1040	18	1500

As the temperature in the kiln rises, the Cone begins to soften and when its fusion point is reached it begins to bend over until its tip touches its base.

The time taken in firing an oven has a great influence on the bending of a Cone. The table given above indicates the temperatures, on two hours firing at the specified temperatures, but if the time of firing is increased, the Cones soften down before the specified temperatures are reached. Thus, Cone 10 would squat at 1200°C if fired for about 2 days in an oven.

This fact shows that Seger Cones do not indicate the exact temperature of the oven although their fusion points are indicated in degrees of temperature. They

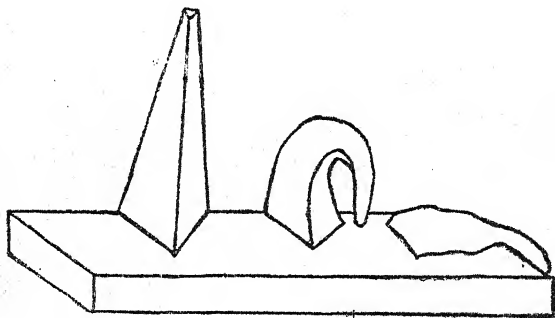


Fig. 49. Seger Cones.

rather serve the purpose of indicating the pyro-chemical effect on the body materials. This is a peculiar virtue and not a fault of the Seger Cones. In fact it is because of this fact that these cones have been so very useful in the clay industries.

In actual firing, time is nearly as much important a factor as the temperature. A prolonged soaking fire at a lower temperature does the same work in maturing a body or a glaze as a quicker fire at a higher temperature. In firing an oven the work done by heat on the

Cones and on the body or the glaze will be nearly proportional to one another. The fireman really wants to know what work the heat has done on the body or the glaze and this is faithfully indicated by the squaring of the Cones irrespective of the actual temperature of the oven. The temperature attained in the oven is of little importance provided the purpose of the firing is accomplished.

The effect of reducing gases is rather the opposite to that of heat. Coal gas or cracked carbon enter the pores of the Cones and form a refractory skin on the surface of the Cone and prevent it from bending even though the interior of the Cone may show sign of melting. In such cases a short washing of the kiln with fresh air will make the Cone to collapse at once. Sulphur gas materially affects the end point of Seger Cones. For obvious reasons it is advisable to make and test these Cones in a public laboratory. Seger Cones were solely manufactured by the Prussian Government at the Royal Porcelain works near Berlin. Later on they were made in the Chemical Laboratory for clay Industries conducted by Dr. H. Seger and E. Cramer at Berlin. In England these Cones are made in Stoke-on-Trent in a well controlled public laboratory. In America the so called Orton Cones are made in Columbus.

Holdcrofts bar pyrosopes resemble the Seger Cones in all respects except that the trial pieces are made in the bar form and not in the form of Cones. They are supported horizontally on special supports and the

critical points are indicated when the bars sag in the centre.

Generally three bars with successive number are kept on a holder and placed in the kiln. Warning is given by the sagging of the most fusible one, the middle one is meant for the actual temperature to be reached, while the third one which sags at a higher temperature than the finishing point required shows whether the kiln has been over fired.

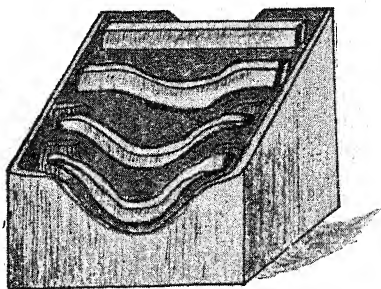


Fig. 50 Holdcrofts bars,

Bullers rings are very much the same as Wedgwoods cylinders except that the trial pieces are made in the form of rings which can be drawn out of the oven easily. The shrinkage of the rings after firing is measured in a special gauge Fig. 51. These rings are used to measure the contraction of the ware in the biscuit ovens and also to check the progress of the firing in the different parts of the oven during firing.

Pyrometers. These are instruments for measuring high temperatures inside furnaces. Unlike the

pyrosopes, the pyrometers can be used over again as these instruments are based on the changes of the physical properties of the materials. Of the various types of these instruments those generally used in the ceramic industries are Electric pyrometers, Radiation pyrometers and Optical pyrometers.

Electric Pyrometers. These can be divided into two classes ; those in which the principle of changes in the resistance of metals with the change in temperature is employed and those making use of the generation of

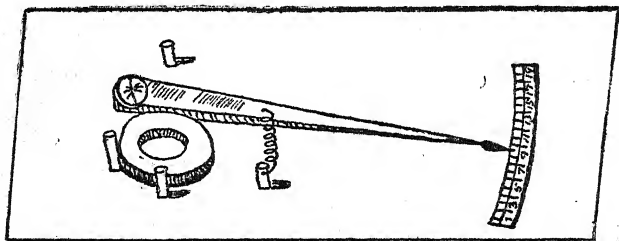


Fig. 51 Buller's ring.

E. M. F. in metals with the rise of temperatures. The former type is known as *Resistance Thermometer* and the latter type as *Thermo-couple pyrometer*.

The foundation on which the modern resistance thermometer rests, is the classical work of Callender in 1887. He found that pure platinum was the best wire to use and that coils of this metal wound round a mica frame would stand temperature up to 1200°C , but it is not safe to expose the wire for a long period beyond 1000°C as the minute disintegration of the

metal at higher temperature would change the resistance of the coil and alter the readings. For temperatures below 300°C pure nickel wire is used. For reading the temperature Callender used the Wheatstone bridge method with compensated lead.

The instrument consists of a resistance coil enclosed in a porcelain sheath and connected to the main box by copper wire. There is one adjustable resistance C by rotating which the resistance of X , can be varied till there is no deflection in the galvanometer G . The dial on the resistance C is so calibrated that when the

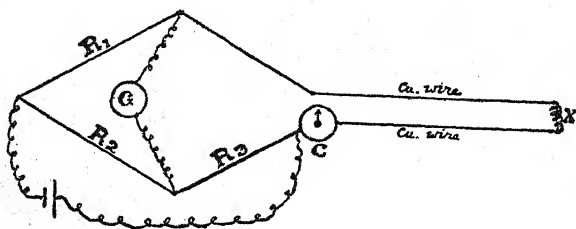


Fig. 52. A Resistance Thermometer.

bridge is in balance the pointer directly indicates the temperature.

This thermometer gives a precision within 1°C when used carefully up to 1000°C but above this temperature the accuracy is less. It can be used with a recorder and it is very helpful in small furnaces for laboratory experiments but not so suitable for rough use in factory furnaces as its calibration may be altered by severe handling or by contamination of the resistance wire with the factory gases.

Thermo-couple pyrometers are based on the thermo-electric properties of metals first discovered by Seebeck in 1820 and generally known as Seebeck Effect. He found that a junction of two different metals is the seat of an E. M. F. and in a complete circuit containing two junctions, there will be two such forces in opposite directions. If one junction is at a higher temperature than the other there will be a resultant E. M. F. which will cause a current to flow in the circuit, the magnitude of which depends upon, the followings factors :—

- (a) The nature of the metals.
- (b) The difference of temperatures of the two junctions.
- (c) The actual temperatures of the two junctions.

Metals used for making thermo-couple should have the following properties :—

- (i) The resistance to corrosion and oxidation.
- (ii) Development of relatively large E. M. F.
- (iii) The E. M. F. produced should increase steadily with the rise of temperature.

There are two types of thermo-couples :—

In the first type only rare metals are used while in the second type the ordinary or base metals are used.

The first type of thermo-couple can be used up to 1400°C while second type is generally used for temperature up to 1100°C .

The two typical couples which are in extensive use are :—

Base metal.

Cu.....58.28 Fe....100.

Ni.....41.72

Up to 1100°C.

Rare metal.

Rh.....10 Pt...100.

Pt.....90

Up to 1400°C.

The advantages of Base metal-couples are :—

- (i) They are much cheaper.
- (ii) They give much greater indications of thermal changes.
- (iii) Thick wire and large couples can be used.

The disadvantages are :—

- (i) The temperature range is limited generally below 1100°C.

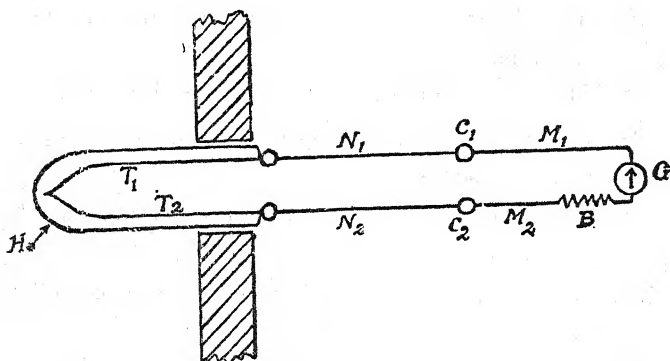


Fig. 53. Thermo-couple pyrometer.

- (ii) They require periodical standardisation.

The thermo-couple are protected in refractory sheath of fused quartz or porcelain to guard the metals against sulphurous fumes and smoky atmosphere. These sheathes should not be thicker than necessary for the adequate protection of the wires as it reduces the sensitiveness of the instrument. There is a

definite *lag* between the time at which any temperature change takes place in the hot oven and the indication of the same on the galvanometer, owing to the time taken by the sheath to transmit the temperature to the thermo-couple. The constructive principle of rare metal thermo-couple pyrometers is shown in fig. 53.

In the above figure H is the hot end of the thermo-couple wires T_1 , T_2 and C_1 , C_2 the cold ends. M_1 , M_2 are the copper cables to connect the instrument to the galvanometer indicator G. B is a heavy resistance inserted in the circuit and known as ballast resistance. N_1 , N_2 are the compensation extensions for the short thermo-couple wires.

The pyrometer is inserted into the kiln through a hole in the wall. If the thermo-couple wires are short, the cold junction is liable to get heated due to radiation from the hot junction, unless it is removed further away from the furnace. To get over this difficulty, the thermo-couple wires are joined at outer ends to *compensation extensions* i.e. two cheaper wires of alloys which are thermo-electrically inter-changeable with the thermo-couple wires, so that in effect the cold junctions are removed to such a distance from the furnace that they will remain practically steady at the temperature of the room. The compensation wires are made of base metals or alloys and they are placed at such a distance from the rare metal couples that they are not exposed to temperatures over 600°C .

With the rise of temperature of the thermo-couple wires their resistance will also vary which are likely to

introduce error in the readings of the indicator scale. To get rid of this difficulty it is necessary to insert into the circuit a large additional resistance called the *ballast resistance* which is made of such materials that do not change in resistance with the change in temperature and it is made so large in comparison with the other resistances in the circuit that any change in those other resistances in the circuit is relatively small and without appreciable effect upon the indicator readings.

Cold junction correction. During the calibration of the indicator scale the cold junction is kept at a constant temperature of 0°C, but in actual practice the temperature of the cold junction would be the temperature of the room. To correct the scale for this change, the pointer of the scale is set to the actual temperature of the room before the indicator is connected to the thermo-couple, because the current generated in the thermo-couple is proportional to the difference of temperature between the hot and the cold junctions.

The current is generally measured by a direct deflection galvanometer or millivoltmeter with a high resistance.

Radiation Pyrometer. This instrument is based on Stefan and Boltzman's law of total radiation. According to this law the total radiation emitted by a hot body varies directly as the difference of the fourth power of the absolute temperatures between the hot body and the cold surroundings.

$$E = K (T_1^4 - T_2^4).$$

All hot bodies radiate heat and the radiant heat follows the same laws as light in reflection from a polished mirror, in absorption in a black body and in transmission through rock salt. Above 500°C the energy radiated from the hot body is partially visible as light and partially invisible as heat. In this system the total energy radiated from a hot body is focussed upon

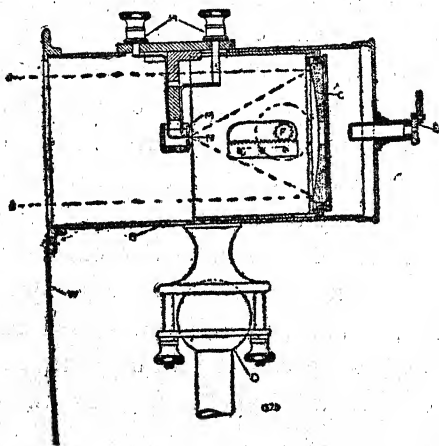


Fig. 54 Fery Radiation pyrometer.

a thermo-couple coated with lamp black which absorbs all the energy as heat and the E. M. F. produced by the thermo-couple is measured to indicate the temperature of the hot body.

In the Fery Radiation Pyrometer the heat rays are received on a concave mirror and brought to a focus on a small thermo-couple. The electromotive force produced by the consequent heating of one junction of the

thermo-couple is measured on an indicating or a recording galvanometer calibrated to give direct readings in temperature. The optical arrangement is illustrated in Fig. 54. The heat rays A from the furnace are received on the concave mirror C, which brings the rays to a focus at N. Looking through the eyepiece E the observer sees an image of the furnace in the small mirror M, and is able to direct and focus the eyepiece E with a telescopic arrangement exactly on the required spot. The sensitive thermo-couple, situated immediately behind a small hole in the mirror M, becomes heated by the rays passing through this hole. The mirror C is made of rustless steel, which can be polished without scratching and is practically unbreakable and untarnishable.

Focussing. An ingenious device enables the operation of sighting and focussing to be easily and quickly performed. The mirror M consists of two small, semi-circular, wedge-shaped mirrors fixed together so that the image of the hot body falling on the mirror is divided into two semi-circular parts round a black centre, the exposed part of the thermo couple. By turning the pinion head F the focussing is so adjusted that the two halves of the image coincide, one above the other.

The size of the aperture of the hot body sighted on, and the distance of the telescope from it, do not, within wide limits, affect the temperature readings; but the body sighted on should be at least 1 inch in diameter for every 2 feet of distance between the telescope and the object, to ensure that its image will

overlap on all sides of the sensitive element in the thermo-couple.

In recording the temperature of ceramic kilns a refractory tube 4 to 5 feet long and 6 ins diam. closed at one end is inserted into the kiln through an opening of the kiln wall. The closed end of the tube takes up the temperature of the furnace and the pyrometer is focussed through the open end.

Chief troubles are :—

- (a) A lag in temperature recorded due to the time taken by the tube to get heated.
- (b) The reflecting mirror may fail to focus directly on the thermo-couple.

These pyrometers are very useful for reading temperatures between 500°C to 1700°C of all types of industrial furnaces.

Optical Pyrometers. These instruments are very convenient for general use and extend in range from a visible red heat (700°C) up to the highest attainable temperature. Owing to the rapidity with which readings can be taken and the ease of sighting upon small objects, these pyrometers are particularly suitable for taking snap readings.

In this system only the visible radiation from the hot body is made use of. The total radiation from a hot body depends not only upon the temperature but also upon the emissive power of the radiating body. A material having the highest possible emissive and absorptive power is known as a *black body*. The emissivity of a black body is taken as one, and all other

materials have emissive power less than one. A black body is experimentally realised by uniformly heating a hollow enclosure and observing the radiation coming out of a small hole in the wall. Muffle furnaces and some annealing furnaces are sufficient approximation to ideal black body. When a material is being heated under black body condition inside an enclosed furnace the total intensity of radiation leaving the material is the same as that emitted by the black body. Optical pyrometers should be sighted when the details of the inside of the furnace would not be visible and the article which is being heated can not be distinguished from its surroundings. If the article is distinguished then either it is hotter (when cooling) or colder (when heating up the furnace) than its surroundings. In the former case the observed temperature would be too low but in the latter case when the furnace walls are brighter, the observed temperature would be rather high. Similarly when a glowing material is sighted in the open, the observed temperature is rather too low and correction must be applied to this reading. This correction is rather too large in the case of a clear molten metal but when a film of oxide is deposited on the surface of the molten metal the error is much reduced. An idea of this error in reading can be obtained when we compare the emissivity of different substances as given below.

Graphite powder	0.95
Carbon	0.85
Iron oxide	0.92
Nickel oxide	0.85

Iron clear metal	0.37
Nickel clear metal	0.36
Porcelain	0.5

Under 'black body' condition *i. e.* when enclosed in an uniformly heated furnace a clear metal would also show correct temperature because the metal would reflect an equivalent amount of energy which it fails to emit at the temperature in an open space.

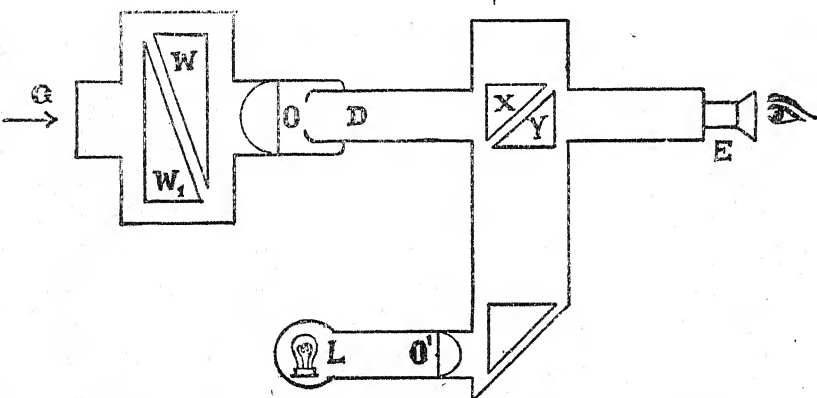


Fig. 55 Fery Optical Pyrometer.

Optical pyrometers of Fery system measure the total intensity of light, obtained from the hot body and compares the intensity with that of a standard light.

The enormous increase in the intensity of light with the rise of temperature has made this easier. The intensity of red light emitted by a hot body at 1500°C is 130 times as great as that emitted by the body at 1000°C. At higher temperatures the increase is much greater in proportion.

In the Fery optical pyrometer the light from the hot source first passes through a pair of wedge shaped prisms W, W_1 and then through an optical system whereby it is polarised and rendered monochromatic. Similarly the light from the standard lamp L is also polarised and rendered monochromatic. The field as seen by the observer through the eye piece E is divided either into two semi-circles or into two concentric rings illuminated from rays from the two different sources. These two images are brought to equal brightness by sliding the observing wedges W, W_1 and the scale attached to the outside ring is calibrated as to indicate the temperature directly. In Cambridge optical pyrometers the scale is engraved on a large circular plate attached to the system of eye-piece which can be adjusted to vary the brightness of the light from the hot source. The large circular plate also serves as a protection of the eyes of the observer from the glare of the furnace.

The accuracy of these instruments depends on the constancy of the light from the standard electric lamp which can be checked against the amyl acetate lamp supplied by the instrument makers.

Wedge Optical Pyrometer. This instrument consists of a brass tube provided with a small telescope $T T$ the objective of which focuses the image of the hot source on a moveable prism P placed inside the tube.

The chief feature of this pyrometer is the glass prism, which from top to bottom is graduated in depths of colour and the prism can be moved by a rack and pinion arrangement with a milled head M . When

commencing to take a reading the prism is so placed that the lightly tinted part, is in the field of vision, and then turning the milled head, the depth of colour is progressively increased until the object just disappears. This point gives the actual temperature directly on the scale.

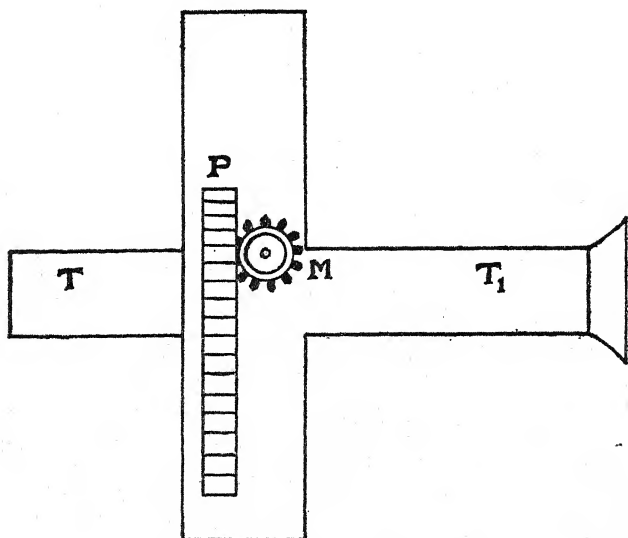


Fig. 56. Wedge optical pyrometer.

This pyrometer has little to get out of order and there is less error due to personal defect. It is cheap and easy to manipulate even by a lay man.

CHAPTER. XII

CERAMIC CALCULATIONS.

1. Moisture content and its significance.

Many of the raw materials used in ceramic industries contain water which may occur in them in two ways:—as water mechanically held, or as water of constitution. The latter form of water forms an integral part of the molecule such as in kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) or as in borax crystals ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$). The chemically combined water is generally constant varying only slightly in some substances such as borax.

The water that is mechanically held in the raw materials is called *moisture* and it varies with the climatic and storage conditions. On account of this uncertain amount of moisture content, it is important to buy the raw materials according to some standard specifications, otherwise financial loss will be incurred; also there will be error introduced in the body mixing unless special precautions are taken in calculating the moisture content in every consignment of raw materials and modifying the recipe accordingly.

To determine the moisture present in a material, a weighed sample is placed in a suitable drier at about 110°C until it comes to a constant weight. The difference between the original weight and that after

drying is the amount of moisture contained in the sample. The percentage is calculated in the ordinary way based on the original weight of the sample.

Suppose we order for china clay with 15 per cent moisture, at the rate of Rs. 50 per ton, but the clay supplied actually contains 20 per cent moisture. Thus we find the loss per ton is Rs. 3, which can not be ignored in big factories where large quantities of raw materials are daily used.

2. Contraction.

When clay bodies are allowed to dry, they shrink or contract in size. This shrinkage is due to the loss of mechanical water due to evaporation, and mainly depends on the amount of water added in the clay during formation and the grain size of the material. Thus a coarse grained sandy clay body shrinks as low as one per cent or less, while a fine plastic clay is found to shrink as much as sixteen per cent in drying. The shrinkage which a clay body undergoes during the drying operation is known as the dry contraction of the body and this may vary according to the temperature of drying. For standard results it is customary to dry the test pieces at 110°C and to cool them in a desiccator.

When a clay body is fired it undergoes a further amount of contraction which increases with the rise of temperature. This second contraction is known as the firing contraction and is mainly due to the elimination of the water of constitution in the clay, organic

impurities in the raw materials, and the incipient fusion of the more fusible constituents of the body. The measurement of this contraction is to be made at definite temperatures and for specific period of firing in order to get comparable results. Clays vary widely in their burning behaviour; one clay may mature at a low temperature while another require a high temperature for maturing.

The measurement of the linear contraction is generally done by marking two points on the test piece at a definite distance apart. The test piece is then dried and the distance between the points measured again. The difference between the original and final lengths represents the dry shrinkage. The test piece is then fired and the firing shrinkage determined in the similar way. The calculation is done in the following way.

Percent linear contraction

$$= \frac{\text{Original length} - \text{Contracted length}}{\text{Original length}} \times 100$$

In the manufacture of vessels designed to hold definite amount of liquid, it is necessary to know the cubical contraction of the clay body. In such cases the volume both before and after contraction can be determined by the following method.

Soak the test piece in kerosin oil and weigh it accurately. Weigh the soaked piece again suspended in the same liquid. If the above two weights are

denoted by W and W_1 respectively and if S denote the sp. gr. of the kerosin used then the true volume of the piece is calculated from the following formula :—

$$\text{Volume} = \frac{W - W_1}{S}$$

In actual practice however it is not always necessary to follow this method as the cubical contraction is approximately three times the linear contraction. The theoretical proof of the above assertion is based on the following mathematical calculations.

Let us consider a cube having originally x mm. side which after contraction becomes $(x-a)$ mm. Therefore the contraction in volume is :—

$$x^3 - (x-a)^3 = x^3 - x^3 + 3x^2a - 3xa^2 + a^3.$$

$$\text{or } 3x^2a - 3xa^2 + a^3.$$

The percentage cubical contraction is therefore :—

$$\begin{aligned} & \left(\frac{3x^2a - 3xa^2 + a^3}{x^3} \right) \times 100 \\ &= \left\{ 3 \frac{a}{x} - 3 \left(\frac{a}{x} \right)^2 + \left(\frac{a}{x} \right)^3 \right\} \times 100 \end{aligned}$$

Now the amount of linear contraction (a) is very small in comparison with the original length (x),

consequently $\left(\frac{a}{x} \right)^2$ and $\left(\frac{a}{x} \right)^3$ are so negligible

quantities that they can be dropped out without introducing much error in the calculation.

Hence the above equation comes out to $3\frac{a}{x} \times 100$, which is three times the percentage linear contraction.

Examples.

(1) A tile body contracts 5.5 per cent from the pressed to the fired state, what size die will be needed for a 6 in. x 6 in. tile ?

(2) A clay body has a drying linear shrinkage of 12 per cent and a burning linear shrinkage of 4 per cent. What should be the size of the mould for a jar, cylindrical in shape, having an inside diameter of 7 inches and the outside diameter of 9 ins. if the jar has to hold exactly one gallon ?

(3) The linear contraction of a slab of a clay from the wet to the fired state is given as 12 per cent. A cube of clay has a volume of 16 c. cs. in the wet state. What will be its volume after firing ?

3. Porosity.

When a clay body is fired, the pore spaces between the fine particles begin to close up with the rise of temperature. The measure of these pore spaces is known as porosity of the body and it depends mainly on the nature of the body mixture and the temperature of firing.

The method of calculating the porosity of a pottery body is based on the following considerations depending on the principles of Archimedes.

Weigh the test piece in air (W).

Soak the test piece in water either under a suction pump or by boiling it for sometime. Weigh it again (W_1).

Suspend the soaked test piece in water connected by a string to one side of a balance and weigh (W_2).

Now $W_1 - W$ = The weight of water which occupies the pore space of the test piece.

And $W_1 - W_2$ = The weight of water displaced by the whole test piece.

Since the specific gravity of water is taken as unity the terms ($W_1 - W$) and ($W_1 - W_2$) give also the respective volumes of the pore space and the test piece as a whole. Therefore the porosity of the test piece is given by the formula.

$$\frac{W_1 - W}{W_1 - W_2}$$

For unfired claywares which get dissolved in water, liquids such as paraffin or kerosin are used but the above formula does not change for that account.

4. Specific gravity.

The ratio between the weight of any volume of a substance and the weight of an equal volume of a standard substance is called the specific gravity of that substance. Water is taken as the standard substance

for the determination of the specific gravity of solids and liquids, and for this reason the sp. gr. of water is taken as unity. In ceramic industry substances like waterglass are valued commercially according to their specific gravity. In slip calculation and for the determination of the 'dry content' of the wet ground materials, the value of sp. gr. is often required. When flint is calcined it expands and the specific gravity falls down so that by the specific gravity determinations the rate of calcination of flint can be controlled.

The specific gravity of liquids is generally determined directly by a hydrometer, which consists of a graduated glass tube having a bulb at the lower end suitably weighted with mercury or fine lead shots, so that the instrument can float vertically in any liquid. This instrument sinks or rises up in the given liquid according to the sp. gr. of the liquid, and graduations on the stem of the instrument read the specific gravity of the liquid.

In determining the sp. gr. of porous solids two different values are generally calculated. The first one in which only the solid matter is taken into consideration is called the *true specific gravity*, whereas, the other value refers to the solid piece as a whole, that is the solid matter with the pore spaces. This latter value is termed the *apparent specific gravity*.

In calculating the above two kinds of sp. gr. the same reasonings are followed as considered in the determination of porosity.

Let W = Weight of the solid piece in air.

W_1 = Weight of the solid piece soaked in water.

W_2 = Weight of the solid suspended in water.

Then $W - W_2$ = the wt. of water displaced by the solid matter alone, that is, the wt. of a volume of water equal to the volume of the solid matter only.

And $W_1 - W_2$ = the wt. of a volume of water equal to the total volume of the solid matter and the pore space.

$$\text{Therefore the True sp. gr.} = \frac{W}{W - W_2}$$

$$\text{And the Apparent sp. gr.} = \frac{W}{W_1 - W_2}$$

5. Dry and wet mixing.

There are two important methods of mixing pottery bodies. In the first one,—the *Dry method* it is usual to mix the raw materials in the same dry condition, as they are brought to the works. The recipes are expressed in weight measures and the different ingredients are weighed out and mixed together with water. In this method proper consideration has to be made for the moisture content of the raw materials in order to get correct weights of the ingredients.

In the second process, the so called *wet method* which is largely practised in England, the ingredients are reduced to a slip or slurry with water and kept separately in blungers until use; and definite volumes

of these slips are then mixed in an ark according to the wet recipe, expressed in inches.

In order to calculate the amount of solid matter or the 'dry content' of the slip or slurry, it is essential to know the consistency of the slip, that is the weight per pint of the same, and the specific gravity of the dry material.

Let W = wt. in grams of one litre of slip.

D = wt. of solid matter or 'dry content' in one litre of slip ; and

S = the specific gravity of the solid.

Now, since the dry material has sp. gravity S , one litre of this solid would weigh $1000 S$ grams. In other words :

D grams of dry material would occupy $\frac{D}{1000 S}$ litre.

Similarly the volume of water contained in one litre

of slip would be $\frac{W-D}{1000}$ litre.

But the total volume of the slip is only one litre.

$$\text{Hence } \frac{D}{1000 S} + \frac{W-D}{1000} = 1$$

$$\text{or } D + WS - DS = 1000 S$$

$$\text{or } D \text{ (grams)} = (W - 1000) \frac{S}{S-1} \dots\dots\dots(i)$$

If W is expressed in ounces per pint as is usual in Great Britain, then the equation (i) which is known as *Brongniarts equation*, would be modified to :—

$$D \text{ (ozs)} = (W - 20) \frac{S}{S - 1} \dots\dots\dots (ii)$$

for one pint of water weighs 20 ozs.

Conversion of wet to Dry recipe.

In the wet method the ingredients are mixed in a common ark having an uniform cross section and the respective heights occupied by different liquid ingredients are measured. In the 'wet recipe' these 'heights' are mentioned together with the consistency of the respective slips.

Now the sp.gr. of the principal pottery materials are numerically very near to each other and do not vary greatly from 2.6. Hence the

factor $\frac{S}{S - 1}$ is practically a constant quantity.

Therefore we can safely say that $D \propto (W - 20)$.

If the height of an ingredient in the mixing ark is 'Y' inches then we get

$$D \propto Y (W - 20)$$

Thus we see that we can get the proportional dry contents, by multiplying the 'heights' of the wet recipe by $(W - 20)$ or $(W - 1000)$ as the case may be according

as the measurements are given in the British or Continental system.

Problem. The wet recipe of an earthen ware body is given as follows :—

14 inches	of ball clay	at 24.5	ozs per pint.				
9	„ „	china clay	„ 25.5	„ „	„ „		
6.5	„ „	flint	„ 31.7	„ „	„ „		
3	„ „	stone	„ 32.2	„ „	„ „		

Report the dry recipe of such a body.

The proportional dry contents of the above recipe are :—

Ball clay,	14(24.5-20)	or 63.	Parts.
China clay,	9(25.5-20)	or 49.5	„
Flint,	6.5(31.7-20)	or 76.0	„
Stone,	3(32.2-20)	or 36.6.	„

Converting the above into percentage composition, we get the recipe.

Ball clay	27.99	Per Cent.
China clay	21.98	„ „
Flint	33.76	„ „
Stone	16.26	„ „

Examples. (1) The weight of paraffin soaked in the pores of a silica brick is 42 grams. If the specific gravity of paraffin is 0.82, find the volume of the pores.

(2) The percentage porosity of a body is 30. In air it weighs 61 grams. Suspended in water it weighs 45 grams. What is the apparent sp. gr. of the body ?

(3) If the specific gravity of flint is 2.65 before calcination and 2.27 after calcination, what is the increase in volume of the flint due to calcination ?

(4) A 100 grams glass cube has a specific gravity 2.6. When weighed suspended in kerosin it weighs 68 grams. what is the sp. gr. of kerosin oil ?

(5) The sp. gr. of a flint slip is 1.54 and that of the dry flint is 2.45. What is the dry content per pint of the slip ?

(6) How much water would you add to 20 gallons of slip with a consistency of 28.5 ozs per pint in order to convert it to the consistency of 26 ozs per pint.

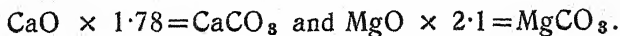
6. Body calculations. There are in practice two ways of chemically analysing clays and clayey mixtures used in body composition. In the one—the *ultimate analysis*, the results are expressed in terms of the individual oxides of inorganic substances present in the mixture. This method gives very accurate results but takes rather too long time to complete a single analysis.

In the other case—the *rational analysis*, the results are expressed in terms of the mineralogical components of the mass, specially the amounts of clay substance, felspar and quartz present. This method of analysis introduces so many inaccuracies that no great reliance can be placed on the results. But the clay workers in general prefer a knowledge of the mineralogical constituents of the body composition, because they have a conception of the properties of the individual minerals. As there is very little hope of improving the method

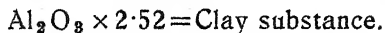
of rational analysis to yield more accurate result, it has been suggested to compute the ideal mineralogical constitution from the ultimate analysis. Such a calculated result is known as the *proximate analysis* and is used now-a-days with some satisfaction, although this method also is the subject of a number of assumptions which limit the sphere of its application.

In calculating the proximate analysis it is usual to assume that the clay substance, feldspar and quartz possess the ideal compositions of kaolinite, orthoclase and pure silica respectively. In practical analysis we know that there are but very few clays which are so pure and almost all feldspars contain soda or lime in more or less amounts. Hence during calculation the sum of the bases, potash, soda, lime, magnesia; is treated as potash and the calculation of feldspar is based on this *total base*, by multiplying it with 5.9. Iron oxide when present in very small amount is computed in the total base but when in larger amount it is reported separately. It is obvious from the above statements that when bases other than potash are in excess this method of calculation is not to be relied upon to any degree of satisfaction. In such cases the method of calculation should be altered according to convenience. For example when soda (Na_2O) is in large excess to potash (K_2O) the ideal feldspar should be calculated on the basis of pure *Albite*— $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. and not on the basis of *Orthoclase*. The factor for converting the total bases into albite is 8.45. In cases where the amounts of CaO or MgO are in

large excess to the amounts of soda and potash, the former two substances should be reported separately as carbonates.



The ideal "Clay substance" is calculated from the residual alumina after calculating the felspar.



The quartz or free silica is then obtained after deducting the amounts of silica present in the felspar and the clay substance, from the total amount of silica.

Some clays like laterite clays contain a high percentage of alumina. In such a case it is necessary to calculate the clay substance on the basis of the silica remaining after the calculation of felspar.



The remaining alumina is reported as *free Alumina*.

With clays, and unfired pottery bodies, the sum of the constituents of a proximate analysis should approximate to 100, and the quantity of each constituent can therefore be regarded as a percentage. With fired bodies this cannot be the case, since the firing causes the elimination of water of constitution, which is estimated in the clay substance, and the sum of the constituents is always greater than 100.

Calculation. Find out the proximate analysis of an earthenware body having the following ultimate analysis :—

SiO ₂	63.00
Al ₂ O ₃	22.00
Fe ₂ O ₃	1.00
K ₂ O	2.15
Na ₂ O	1.02
MgO	0.24
CaO	0.81
Loss	9.82
				<hr/>
				100.04

The sum total of all the bases in this case is 4.22 and as K₂O is in excess to all other bases the felspar should be calculated on the *orthoclase* basis.

Hence total "ideal" felspar = $4.22 \times 5.9 = 24.9$ parts. Now 556 parts of orthoclase contain 102 parts of Al₂O₃ and 360 parts of SiO₂. Therefore 24.9 parts of this felspar should contain 4.56 parts of Al₂O₃ and 16.11 parts of SiO₂.

The Al₂O₃ remaining after the removal of felspar therefore = $22.0 - 4.56$ or 17.44. Hence "clay substance" = 17.44×2.52 or 44.12 parts. Now 258 parts of clay substance contain 120 parts of SiO₂ therefore 44.12 parts will contain 20.52 parts of SiO₂. Hence "Quartz" or free silica = $63 - (16.11 + 20.52)$ or 26.37.

Hence the proximate analysis of the same body :—

Clay substance	=	44.12
Ideal orthoclase	=	24.90
Quartz	=	26.37
Ferric Oxide	=	1.00

7. Glaze Calculations. There are three ways of expressing the composition of a ceramic glaze. (a) The *ultimate analysis* or the usual way of expressing the percentages of the active oxides as obtained directly from a chemical analysis of the dry material. (b) The *recipe* or batch-weight, showing the amounts of individual raw materials used in the composition of the glaze. (c) The *molecular formula*. This is a conventional method of showing the proportional relationship between the active oxides present in the glaze composition. This particular form is largely used by ceramists as it conveys much information of directly practical value to an experienced man.

Conversion of Ultimate analysis into molecular formula.

Problem. Express the following ultimate analysis of an earthenware glaze in the form of a molecular formula.

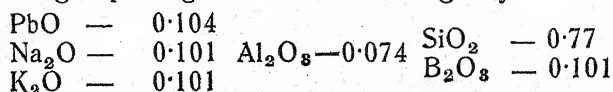
SiO_2	=	46.23
B_2O_3	=	7.09
Al_2O_3	=	7.63
PbO	=	23.27
Na_2O	=	6.28
K_2O	=	9.52

Multiplying the amounts of the individual oxides by their respective molecular weights we get the molecular proportions of these oxides, as shown in the following table.

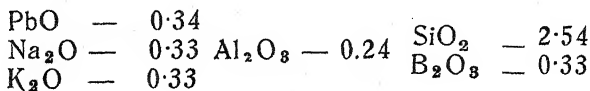
Chemical constituents.	Percentage composition.	Molecular weight.	Molecular Proportion.
SiO_2	46.23	60	0.77
B_2O_3	7.09	70	0.101
Al_2O_3	7.63	102	0.074
PbO	23.27	223	0.104
Na_2O	6.28	62	0.101
K_2O	9.52	94	0.101

In representing the molecular formula of a glaze, the silica and boric oxides are grouped together and referred as *acidic oxides*, since they combine with other basic constituents present in the glaze, to form chemical compounds. The alumina is treated as a neutral or *amphoteric* body and is kept separate. The remaining other oxides are grouped together and called the *bases*.

Following the above rules, the results of column 4, can be grouped together in the following way :—

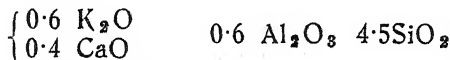


Now, it is customary for general convenience to refer the sum of the bases as unity, modifying the other constituents accordingly. Thus, by multiplying all the above numbers by 3.3, so that the total of the bases become one, the molecular formula of the given glaze is derived as follows :



Conversion of a molecular formula into a recipe.

Problem. Convert the following formula into a recipe.



Use felspar, whiting and flint for compounding the above glaze. In order to introduce 0.6 molecule of K_2O we require 0.6 molecule of orthoclase felspar with ideal composition. It will also bring 0.6 molecule of Al_2O_3 and 3.6 molecule of SiO_2 . Now, the molecular weight of orthoclase is 556, so that 0.6 molecule of it is equivalent to 333.6 parts by weight. Similarly 0.4 molecule of whiting CaCO_3 will introduce 0.4 molecule of CaO which is equivalent to 40 parts of whiting by weight as shown in the following table. The remaining 0.9 molecule of SiO_2 is taken from 0.9 molecule of flint which is equivalent to 54 parts by weight. In the last column

is calculated the percentage recipe from the result of column 4.

Materials	Molecular weight	Molecular part.	Recipe	K ₂ O	CaO	Al ₂ O ₃	SiO ₂	Percentage recipe.
Felspar	556	0.6	333.6	0.6	0.6	3.6	78.01
Whiting	100	0.4	40.0	0.4	9.35
Flint	60	0.9	54.0	0.9	12.63
Total.			427.6	0.6	0.4	0.6	4.5	99.99

The calculation of the formula from the recipe is just the reverse of the foregoing considerations. The procedure is easily followed from the following example.

Problem. Calculate the formula of the following raw glaze recipe.

Felspar	42
Whiting	18
Flint	25
China clay	12

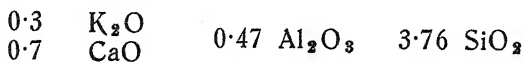
Now, dividing the amounts of each ingredient by their respective molecular weights, we get their molecular equivalents.

Felspar	$42 \div 556 = 0.075$	molecules.
Whiting	$18 \div 100 = 0.180$	"
Flint	$25 \div 60 = 0.416$	"
China clay	$12 \div 258 = 0.046$	"

Construct a table and place the amount of each oxide contained in each constituent in the proper column as shown below :

Constituents	Molecular part.	K ₂ O	CaO	Al ₂ O ₃	SiO ₂
Felspar.	0.075	0.075	...	0.075	0.450
Whiting.	0.180	...	0.180
Flint.	0.416	0.416
China clay.	0.046	0.046	0.092.
	...	0.075	0.180	0.121	0.958.

Now arranging the bases and acids separately in the conventional way and making the bases unity, we get :—



Fritted glazes.

When soluble materials such as borax, soda ash, pearl ash etc. are used in the glaze mixture, these must be first fritted or made into an insoluble glass and then introduced into the glaze. The frit composition should be so made that it fuses easily at low temperature and the molten glass is not too viscous.

If the frit is too refractory, there is an increasing tendency for the more volatile materials in it such as alkalis, lead oxides, or boric acid to be driven off, due to the high temperature required in smelting the frit.

In order to keep the frit within the limits of easy fusion, the ratio of the total acid molecules to the basic molecules should never be less than 1 to 1 and not more than 3 to 1.

The acid elements of the frit should always contain some silica when boric oxide is also present. The ratio of SiO_2 to B_2O_3 should be at least 2 to 1.

Alumina tends to form a very viscous frit which is very difficult to pour out. Hence the alumina content must not greatly exceed 0.2 molecule.

The following problems will illustrate the methods used for the calculations of fritted glazes.

Problem. Express the given recipe by means of a formula assuming ideal composition for each ingredient.

Frit mixture.

Borax	...	60
Soda ash	...	10
China clay	...	25
Whiting	...	20
Flint	...	35

Mill mixture.

Frit	...	100
White lead	...	60
Flint	...	40

Let us first consider the loss in weight of the frit mixture due to the smelting operation.

A table for the conversion factors is given in the appendix.

60 parts of borax will give after fritting.

60×0.529 or 31.74 parts of permanent oxide.

10 parts of soda ash will give

10×0.585 or 5.85 parts of permanent oxide.

25 parts of china clay will yield

25×0.86 or 21.5 parts of permanent oxide.

20 parts of whiting will yield

20×0.56 or 11.2 parts of permanent oxide.

35 parts of flint will give

35×1 or 35.0 parts of permanent oxide.

Hence 150 parts of frit mixture will give 105.29 parts of permanent oxides.

We find that in the mill mixture only 100 parts of frit is required. This frit is derived by smelting 142 parts of frit mixture which is made up from :

$$\frac{60}{150} \times 142 = 56.8 \text{ parts of borax.}$$

$$\frac{10}{150} \times 142 = 9.46 \text{ parts of Soda ash.}$$

$$\frac{25}{150} \times 142 = 23.66 \text{ parts of China clay.}$$

$$\frac{20}{150} \times 142 = 18.93 \text{ parts of whiting.}$$

$$\frac{35}{150} \times 142 = 33.13 \text{ parts of Flint.}$$

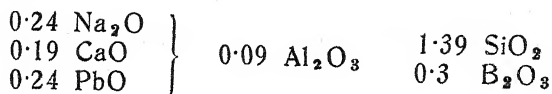
Thus the total amount of various ingredients used in the whole glaze are :

<i>Ingredients</i>		<i>Frit mixture</i>		<i>Mill mixture</i>		<i>Total</i>
Borax	...	56.8	...	—	...	56.8
Soda ash	...	9.46	...	—	...	9.46
China clay	...	23.66	...	—	...	23.66
Whiting	...	18.93	...	—	...	18.93
Flint	...	33.13	...	40	...	73.13
White lead	...	—	...	60	...	60.00

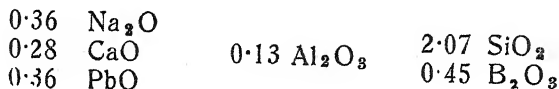
We can now calculate the formula according to the tabular method shown below.

Materials	Molecular weight	Molecular part.	Na ₂ O	CaO	PbO	Al ₂ O ₃	SiO ₂	B ₂ O ₃
Borax	382	0.15	0.15	—	—	—	—	0.3
Soda ash	106	0.09	0.09	—	—	—	—	—
China clay	258	0.09	—	—	—	0.09	0.18	—
Whiting	100	0.19	—	0.19	—	—	—	—
Flint	60	1.21	—	—	—	—	1.21	—
White lead	775	0.08	—	—	0.24	—	—	—
	—	—	0.24	0.19	0.24	0.09	1.39	0.3

Arranging the oxides in the usual way we get :

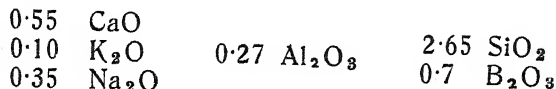


Now bringing the bases into unity, the above formula becomes :

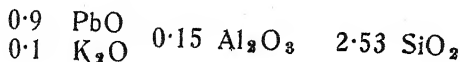


Problem. Convert the following frit formula into a fritted glaze recipe.

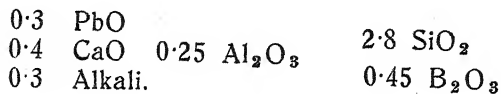
Borax frit :—



Lead frit :—



Glaze body :—



In order to make the borax frit we have to use borax, felspar, flint and china clay in such proportions that each ingredient will bring the required amount of

oxides as given in the above formula. Thus 0.35 molecule of borax crystal would introduce into the frit mixture 0.7 equivalent of B_2O_3 and 0.35 equivalent of Na_2O . Similarly 0.1 molecule of felspar would introduce 0.1 equivalent of K_2O as well as 0.1 equivalent of Al_2O_3 and 0.6 equivalent of SiO_2 . The remaining portion of Al_2O_3 and SiO_2 are taken from china clay and flint. The CaO is introduced from whiting, as shown below.

Materials	Molecular weight	Parts by weight.	CaO	K_2O	Na_2O	Al_2O_3	SiO_2	B_2O_3	Fritted wt.
Borax	382	133.7			0.35			0.7	70.72
Felspar	556	55.6		0.1		0.1	0.6		55.6
Whiting	100	55.0	0.55						30.8
Flint	60	102.6					1.71		102.6
China clay	258	43.86				0.17	0.34		37.71
...		390.76	0.55	0.1	0.35	0.27	2.65	0.7	297.43

In the above table the last column gives the fritted weight of the mixture. That is to say, 390.76 grams of the mixture become after the fritting operation 297.43 grams only.

The lead frit is prepared in similar way using red lead felspar, flint and china clay. The calculation is

done exactly as before and the results are tabulated below.

Calculation of the glaze body :—

In order to introduce 0.45 equivalent of B_2O_3 in the glaze body, we are to take $\frac{297.43}{0.7} \times 0.45$ or 191.2 grams of borax frit.

Materials	Molecular wt.	Parts by wt.	PbO	K ₂ O	Al ₂ O ₃	SiO ₂	Fritted wt.
Red lead	685	205.2	0.9				200.4
Felspar	556	55.6		0.1	0.1	0.6	55.6
Flint	60	109.8				1.83	109.8
China clay	258	12.9			0.05	0.1	11.09
	—	383.5	0.9	0.1	0.15	2.53	376.89.

191.2 gram of borax frit also brings the following ingredients with it.

$$\frac{191.2}{297.43} \times 2.65 \text{ or } 1.703 \text{ equivalent of SiO}_2$$

$$\frac{191.2}{297.43} \times 0.27 \text{ or } 0.173 \text{ equivalent of Al}_2\text{O}_3$$

$$\frac{191.2}{297.43} \times 0.55 \text{ or } 0.353 \text{ equivalent of CaO}$$

$$\frac{191.2}{297.43} \times 0.1 \text{ or } 0.064 \text{ equivalent of } K_2O$$

$$\frac{191.2}{297.43} \times 0.35 \text{ or } 0.225 \text{ equivalent of } Na_2O$$

Thus the total alkalis introduced is only 0.289, but we require 0.3 equivalent. The difference of 0.011 is now introduced from the lead frit.

In order to introduce 0.011 equivalent of alkalis in the form of K_2O , we have to take :—

$$376.89 \times \frac{0.011}{0.1} \text{ or } 41.45 \text{ grams of lead frit.}$$

This amount of lead frit also brings with it :—

$$\frac{41.45}{376.89} \times 0.9 \text{ or } 0.099 \text{ equivalent of } PbO.$$

$$\frac{41.45}{376.89} \times 0.15 \text{ or } 0.016 \text{ equivalent of } Al_2O_3$$

$$\frac{41.45}{376.89} \times 2.53 \text{ or } 0.278 \text{ equivalent of } SiO_2$$

Now taking both the frits together we are introducing into the glaze mixture the following permanent oxides.

	PbO	CaO	K ₂ O	Na ₂ O	Al ₂ O ₃	SiO ₂	B ₂ O ₃
Borax frit.	—	0.353	0.064	0.225	0.173	1.703	0.45
Lead frit.	0.099	—	0.011	—	0.016	0.278	—
	0.099	0.353	0.075	0.225	0.189	1.981	0.45

The remaining oxides are added into the glaze mixture in the raw state. Thus we have to add further the following oxides.

0.201 PbO or $\frac{775}{3} \times 0.201$ or 51.9 as white lead.

0.047 CaO or 100×0.047 or 4.7 as whiting.

0.061 Al₂O₃ or 258×0.061 or 15.7 as china clay.

0.819 SiO₂ or 60×0.819 or 49.14 as flint.

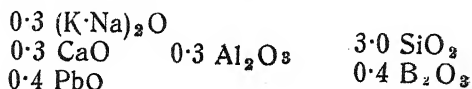
Therefore the recipes of the glaze and two frits are as given below.

<i>Borax Frit.</i>			<i>Lead Frit.</i>		
Borax crystal	...	133.7	Red lead	...	205.2
Whiting	...	55.0	Flint	...	109.8
Felspar	...	55.6	Felspar	...	55.6
Flint	...	102.6	China clay	...	12.9
China clay	...	43.86			

Glaze mixture.

Borax frit.	...	191.20
Lead frit	...	41.45
White lead	...	51.9
Flint	...	49.14
China clay	...	15.7
Whiting	...	4.7

Example. Convert the formula :—



into a fritted glaze recipe using a mixed stone with the following analysis.

SiO ₂	72.15
TiO ₂	0.20
Al ₂ O ₃	16.30
Fe ₂ O ₃	1.45
MgO	0.20
CaO	1.68
K ₂ O	5.11
Na ₂ O	1.56
Loss	1.20
			<hr/>
			99.85

Following the rules of fritting given before, we may divide the glaze formula into two parts—

(a) Frit mixture, and (b) Mill mixture. For the frit mixture we take the following ingredients.

Alkalies—0.3		B ₂ O ₃ —0.4
CaO —0.3	Al ₂ O ₃ —0.2	SiO ₂ —0.8 or more
PbO —0.4		

In order to introduce 0.4 B₂O₃ in the above frit mixture, we may use 0.2 molecules or 76.4 parts of borax crystals. This borax will also bring 0.2 Na₂O. Hence the remaining alkalies in the frit will have to be supplied from the given stone.

Dividing the ultimate analysis of the stone by the molecular weights of the respective oxides, we get—

$$\text{SiO}_2 - 72.15 \div 60 = 1.2 \text{ molecules.}$$

$$\text{Al}_2\text{O}_3 - 16.30 \div 102 = 0.16 \quad ,,$$

$$\text{CaO} - 1.68 \div 56 = 0.03 \quad ,,$$

$$\text{K}_2\text{O} - 5.11 \div 94 = 0.054 \quad ,,$$

$$\text{Na}_2\text{O} - 1.56 \div 62 = 0.025 \quad ,,$$

From the above calculation we find that 99.85 parts of the stone bring 0.079 molecules of alkalies. Hence to introduce 0.1 molecule of alkalies we want 126 parts of the stone. This stone also brings the following amounts of different oxides.

$$\text{SiO}_2 - 1.2 \times \frac{126}{99.85} \text{ or } 1.5 \text{ molecules.}$$

$$\text{Al}_2\text{O}_3 - 0.16 \times 1.26 \text{ or } 0.2 \text{ molecules.}$$

$\text{CaO} - 0.03 \times 1.26 \text{ or } 0.04 \text{ molecules}$ and small amounts of other impurities like TiO_2 , Fe_2O_3 , MgO etc. To introduce the remaining amount or (0.3—0.04) CaO , we require 0.26 molecule of lime stone or 26 parts.

The 0.4 PbO may be introduced from $\frac{685 \times 0.4}{3}$ or 91.3

parts of Red lead.

Hence the composition of the frit mixture is :—

Borax crystals	...	76.4 parts.
Stone	...	126.0 ,,
Lime stone	...	26.0 ,,
Red lead	...	91.3 ,,
Total	...	<u>319.7</u>

On fritting, 319.7 parts of this frit mixture will yield ;—

$$76.4 \times 0.529 = 40.4$$

$$126 \times 0.98 = 123.5$$

$$26 \times 0.56 = 14.5$$

$$91.3 \times 0.977 = 91.2$$

269.6 parts of frit.

Now we are to add in the mill mixture 0.1, Al_2O_3 and 1.5 SiO_2 . This we can introduce easily from China clay and quartz powder, by using 25.8 parts of the former and 78 parts of the latter.

Hence the recipe for the mill mixture :—

Frit	269.6 parts.
Quartz	78.0 „
China clay	25.8 „

Low solubility glazes. The toxic effect of lead in human bodies was not so well known in older days as now, and prior to 1904 there was no restriction on the use of lead compounds in glazes and enamels. In the year 1904 an enquiry was started to formulate regulations in order to prevent lead poisoning from the use of glazed and enamelled wares containing lead compounds. According to these regulations no glaze or frit should yield to a solution of HCl containing 0.25 per cent of acid, more than five per cent of its dry weight of a soluble lead salt calculated as PbO .

As it is not practicable to test each glaze in a laboratory to determine its suitability under the

above mentioned regulations, Dr. T. E. Thorpe proposed an empirical rule which gives a very fair indication of the low solubility of the glaze or frit. According to this rule which is generally known as *Thorpe's Ratio*—the sum in molecular parts of the bases including alumina is calculated as lead monoxide and divided by the sum of the acids calculated as silica. In those cases, where the quotient is less than 2, the glaze will probably pass the Government Solubility Test.

Expressed mathematically we get—

$$\frac{\text{Sum of Bases including alumina}}{\text{Sum of acids}} \times \frac{223}{60} = 2 \text{ or less.}$$

Dr. J. W. Mellor made an amendment to Thorpe's ratio by suggesting that the multiplication by $\frac{223}{60}$ can be avoided by the following modification.

$$\frac{\text{Sum of the bases including alumina}}{\text{Sum of the acids}} = \frac{60}{223} \times 2$$

$$= 0.5 \text{ or less.}$$

It should be emphasized here that these rules merely indicate the probability of passing the solubility test of a glaze or frit because the low solubility of a glaze depends on various other factors.

Lead frit containing much borax, dissolves very easily. Frits high in alumina dissolve very slowly in the acids. A very low soluble frit can be made fairly soluble by grinding it finer. Low solubility frits dissolve but very slowly in the gastric juice and have

plenty of time, to pass out of the human system. It is a common practice to build up the glaze from two frits. One of these contains all the borax while the other contains all the lead together with sufficient silica and Al_2O_3 to give the low solubility ratio.

8, **Elutriation and Standard surface factor.** The importance of the fineness of ground materials in ceramic industry is recognised now-a-days more than before. The size of the particles of raw materials has an important bearing on the properties of the finished products. It has been found in practice that the grain size of such materials as flint, quartz and felspar, is more important than the quality of the material.

The most common method whereby the size of particles of ground materials can be determined is the use of sieves; this method is quite satisfactory except in cases of extremely fine grained materials. British standard sieves are made such that the diameters of the wires used are very nearly equal to the width of the mesh. Thus in sieve No. 100, there are one hundred apertures per linear inch and an equal number of wires between them, so that the width of each aperture will be 0.005 in or 0.127 mm. American standard sieves are slightly different from those of British ones. In this scale, like the British one, each sieve is designated by a number which indicates the number of meshes per linear inch but unlike the British scale the width of the apertures follows a different rule which is based on a definite mathematical relation. The ratio of the size of the aperture in a sieve to that in the sieve having the

next larger aperture varies with the ratio of the fourth root of 2 which is as 1 : 1.1892. Sieve No. 18 is the basis having 1 mm. aperture. Thus in sieve No. 100 the width of each hole is 0.0059 inch or 0.149 mm. In the Continental sieves, the sieve number indicates the number of holes per square centimetre. Thus sieve No. 100 contains one hundred apertures per square centimetre or ten holes per linear centimetre, so that each hole is nearly 0.5 mm. or 0.0196 inch wide.

When the ground material is very fine, even the finest sieve is not adequate for determining the size of the fine particles. In such cases the fine particles are divided into several fractions according to their sizes by a process known as *elutriation*. The principle on which this process is based is explained as follows,

When a given particle is dropped into still water, the particle will sink down with a speed depending on its size, sp. gr. shape and the nature of its surface. When ceramic materials are ground very finely the shape of the particles become more or less spherical and the nature of the surface uniform. Hence the main factors which determine the speed of fall of the particles are the size and sp. gr.

Now if water is made to flow up with gradually increasing speed, the particles will first remain stationary when the speed of the rising water is equal to that of the falling particle but as the speed of the water increases the particle will be carried upwards. Hence if we can determine the speed of the water flow we can calculate the size of the particle from the equation.

$$\text{Velocity} = 104.7 (S-1)^{1.57} d^{1.57}$$

Where S = sp. gr. and d = mean diameter.

By using different speed of water, it is possible to separate a given powder into a number of fractions whose mean diameters we can calculate from the above equation.

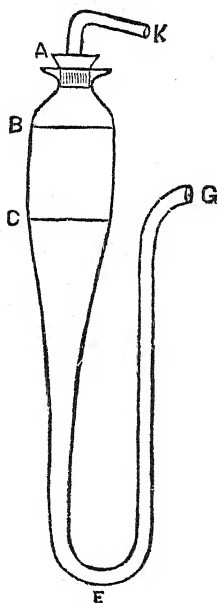


Fig. 57. Schoene's Elutriator.

Depending on this principle E. Schoene invented an apparatus to separate finely powdered substances into different fractions according to the size of the grains. The apparatus consists of a bent tube AEG fitted with a stopper at A, provided with a narrow

bent tube AK. The broadest portion of the apparatus BC is cylindrical but above and below this portion the tube narrows. Water enters at G and leaves the apparatus at K. The speed of water flowing through the apparatus is determined in the following way. The apparatus is filled with water up to the lower level of the cylindrical portion BC. Then a given volume of water 'v' is poured into the cylinder and the rise of level 'h' is marked. From this volume and height of water, the cross-section of the cylinder is calculated.

$$\text{Cross section} = \frac{v}{h}$$

Now if we want that water should flow through the cylindrical portion of the tube at a speed 's' per minute, then the volume of water 'V' flowing out of the tube at K, per minute would be :—

$$V = \frac{v}{h} \cdot s$$

This V is determined by collecting the water flowing out of the apparatus in a measuring cylinder. There are various other types of modified elutriators placed in the market in recent years but the underlying principle in all these apparatus is the same.

The total surface area exposed by one gram of finely ground material is called the *Standard Surface factor*.

The calculation of the same is based on the assumption that the solid particles of very finely ground

materials are spherical in shape. The general formula used for this calculation is derived from the following consideration.

Let us take one fraction obtained from an elutriation analysis of a fine grained material. The diameters of the particles within this fraction vary between two known extreme limits. The average size of these particles is calculated from the formula :—

$$d = \sqrt[3]{\frac{(d_n + d_1)(d_n^2 + d_1^2)}{4}}$$

Where the diameters of the particles vary between two extreme values d_n and d_1 .

The average volume of the particles is calculated from :

$V = \frac{1}{6} \pi d^3$ and the average weight $w = \frac{1}{6} \pi d^3 s$; where s is the specific gravity of the material.

Now, if the total weight of the whole fraction is W and the number of particles in the fraction is N , then

$$N = \frac{W}{\frac{1}{6} \pi d^3 s} = \frac{6W}{\pi d^3 s}$$

The surface of a spherical particle is $= \pi d^2$. Therefore the total surface of the fraction containing N

$$\text{particles} = \frac{6W}{\pi d^3 s} \pi d^2 \text{ or } \frac{6W}{ds}$$

If we have a number of such fractions the weights of which are W_1, W_2, W_3, \dots and each fraction has a mean diameter d_1, d_2, d_3, \dots respectively, the total surface is represented by the formula :—

$$\frac{6}{s} \left\{ \frac{W_1}{d_1} + \frac{W_2}{d_2} + \frac{W_3}{d_3} + \dots \right\}$$

The standard surface factor is calculated from the above formula by expressing the total weights of $W_1 + W_2 + W_3 + \dots = 1$.

The result is expressed in square centimetre.

In order to elutriate the common pottery materials and find their standard surface factor, Mellor has suggested the following procedure which is generally followed in England for standard results.

A. The materials passing through a 120's standard lawn be separated into three fractions.

- (i) *Dust*, or granules below 0.01 m.m. in diameter which are carried away by a stream of water with a velocity of 0.18 m.m. per second.
- (ii) *Silt*, or granules between 0.01 and 0.063 m.m. in diameter which are left behind in the elutriator after the first fraction is removed.
- (iii) *Grit*, or granules between 0.063 and 0.107 m.m. which is retained on a 200's lawn.

In particular cases the finest fraction may be subdivided further into two or more subgroups.

The standard surface factor is computed from the formula deducted before.

It is advisable to use the flint or quartz in slop state, for when dried, the fine particles clog together and give wrong results. When using natural clays it is usual to deflocculate them with suitable electrolytes.

EXERCISE.

1. The mill-mixing of a glaze is :—

Borax frit	...	400 parts.
White lead	...	150 parts.
Stone	...	80 „
Flint	...	70 „

How would you turn the above glaze into a low solubility glaze ?

2. How many gallons of water run off a filter-press yielding one ton of plastic clay containing 25 per cent moisture, if the slip has been pumped in at the weight of 26 ozs. per pint.

3. An earthenware body is made up of :—

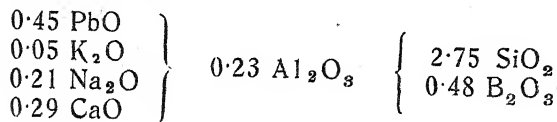
16-in. of Ball Clay at	23 ozs. to the pint.
8-in. of China „ „	26 ozs. „
6-in. of Flint. „	31 ozs. „
3-in. of Stone „	30 ozs. „

For the purpose of this question the specific gravity of all the materials is to be taken as the same. Calculate ; (A) the percentage composition, dry ; (B) the approximate silica composition ; (C) What will be the weight of a pint of the slip in the mixing arc when it is thoroughly blunged ; (D) discuss shortly the probable working qualities of the body and say what kind of ware you would expect it to make.

4. Give the formula for the following recipe of a fritted glaze :—

<i>Frit.</i>		<i>Mill.</i>	
Borax	60.	Frit	300.
Quartz	56.	Quartz	16.
Soda Ash	8.	China clay	22.
Felspar	52.		
White Lead	107.		
Whiting	22.		

5. After mixing a charge of earthenware slip it was noticed that the pint can be used for checking the slop weights had been dented all the time, and could hold only 19 fluid ounces. Will this alter the body composition? If so, in what way can this mixing be corrected.
6. Calculate a recipe for a low solubility glaze showing why you think the glaze will comply with the regulations :—



APPENDIX.

TABLE I. Conversion factors for raw to fritted weights, for materials mainly used in pottery glazes.

Materials.	Factors.	Oxides after fritting.
1. Alum. comn	0.206	$K_2O, Al_2O_3.$
2. Aluminium hy- drate	0.654	Al_2O_3
3. Borax cryst	0.529	$Na_2O, 2B_2O_3$
4. Boric Acid	0.565	B_2O_3
5. Borocalcite	0.820	$CaO, 2B_2O_3$
6. Barium carbonate	0.777	$BaO.$
7. Barium sulphate	0.657	$BaO.$
8. Calcium carbonate	0.560	$CaO.$
9. Calcium sulphate	0.325	$CaO.$
10. China clay	0.860	$Al_2O_3, 2SiO_2$
11. Red lead	0.977	$3PbO.$
12. White lead	0.863	$3PbO.$
13. Magnesium car- bonate	0.479	$MgO.$
14. Soda ash	0.585	$Na_2O.$
15. Soda cryst	0.217	$Na_2O.$
16. Soda nitre	0.364	$Na_2O.$
17. Pearl ash	0.681	$K_2O.$
18. Potash nitre	0.465	$K_2O.$

TABLE 2. Substances used in pottery manufacture. Their chemical compositions, molecular weights, and melting points.

DC=Decompose. F=easily fusible. I.F.=Infusible.

Name.	Formula	Mol. wt.	M.P.°C.
Alabaster ...	<i>see</i> Gypsum ...	172	...
Albite ...	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	524	1200
Alum. Potash ...	$\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$...	948	92
Alumina ...	Al_2O_3 ...	102	2050
Aluminium ...	Al ...	27	657
Alumina hydrate ...	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$...	156	300
Anorthite ...	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	278	1300
Antimony ...	Sb ...	120	...
Antimony oxide ...	Sb_2O_3 ...	288	...
Arsenious oxide ...	As_2O_3 ...	198	200
Barium Carbonate ...	BaCO_3 ...	197.4	795
Baryta ...	BaO ...	153.4	...
Barytes ...	BaSO_4 ...	233.4	1500
Bauxite ...	$\text{Al}_2\text{O}_3 \cdot 2\text{Al}_2(\text{OH})_6 \cdot x\text{Fe}_2(\text{OH})_6$	1820
Bismuth Nitrate ...	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$...	484	73
Bismuth ...	Bi ...	208	269
Bismuth oxide ...	Bi_2O_3 ...	464	700
Bone ash ...	$\text{Ca}_3(\text{PO}_4)_2$...	310	...
Boracite ...	$6\text{MgO} \cdot \text{MgCl}_2 \cdot 8\text{B}_2\text{O}_3$	190	...
Borax cryst... ..	$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$	382	878
Boric acid ...	H_3BO_3 ...	62	185
Borocalcite ...	$\text{CaO} \cdot 2\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	404	...
Boric oxide... ..	B_2O_3 ...	70	577
Cadmium ...	Cd ...	112.4	321
Cadmium sulphide	CdS ...	144.4	D.C 828
Calcite ...	CaCO_3 ...	100	2570

Name	Formula	Mol. wt.	M.P. °C
Calcium oxide ...	CaO ...	56	3000
Calcium silicate ...	CaO. Si ₂ ...	116	1400
Calcium sulphate ...	CaSO ₄ . 2H ₂ O ...	136	130?
Carborundum ...	SiC ...	40.3	2700
Chert ...	Impure SiO ₂	1700
China clay ...	Al ₂ O ₃ . 2SiO ₂ . 2H ₂ O ...	258	1770
Chrome alum ...	Cr ₂ (SO ₄) ₃ . K ₂ SO ₄ . 24H ₂ O. ...	998	
Chromic oxide ...	Cr ₂ O ₃ ...	152	
Chromium ...	Cr. ...	52	1520
Cobalt ...	Co. ...	59	1490
Cobalt chloride ...	Co ₂ Cl ₆ ...	331	
Cobalt carbonate ...	CoCO ₃ ...	119	
Cobaltic oxide ...	Co ₂ O ₃ ...	166	
Cobaltous oxide ...	CoO ...	75	
Cobalt phosphate ...	Co ₃ (PO ₄) ₂ . 8H ₂ O ...	511	
Cobalt silicate ...	2CoO. SiO ₂ ...	210	
Corundum ...	Al ₂ O ₃ Cryst ...	102	2000 1083 1065
Copper ...	Cu. ...	63	
Cupric oxide ...	CuO ...	79	
Cuprous oxide ...	Cu ₂ O ...	143	
Copper sulphate ...	CuSO ₄ . 5H ₂ O ...	249	240
Cryolite ...	Al ₂ F ₆ . NaF ...	420	977
Dolomite ...	Ca. Mg. (CO ₃) ₂ ...	Varies	D.C.
Felspar ...	RO. Al ₂ O ₃ . 2-6SiO ₂ ...		
Ferric chloride ...	Fe ₂ Cl ₆ ...	325	Below
Ferric hydroxide ...	Fe ₂ (OH) ₆ ...	214	280E.
Ferric oxide ...	Fe ₂ O ₃ ...	160	1550
Ferric sulphate ...	Fe ₂ (SO ₄) ₃ . 9H ₂ O ...	562	.
Ferrous oxide ...	FeO ...	72	
Ferrous sulphate ...	FeSO ₄ . 7H ₂ O ...	278	280
Ferrous sulphide ...	FeS ...	88	
Fluorspar ...	CaF ₂ Native... ...	78	1330

Name	Formula	Mol. wt.	M.P.°C
Galena ...	PbS Impure ...	239	
Glaubers salt ...	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$...	322	150
Gold ...	Au ...	197	1063
Gold chloride ...	AuCl_3 ...	303.5	
Gypsum ...	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$...	172	136
Heavy spar...	Barytes ...	233.4	1550
Iron pyrite ...	FeS_2 ...	119.48	1170
Kaolin ...	see china clay
Lead ...	Pb ...	207	327
Lead acetate ...	$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$...	379	
Lead antimoniate ..	$\text{Pb}_3(\text{SbO}_4)_2$...	989	
Lead Chromate ...	PbCrO_4 ...	323	
Lead sulphide ...	PbS ...	239	
Lime ...	CaO ...	56	3000
Litharge ...	PbO ...	877	877
Magnesia ...	MgO ...	40.3	2800
Magnesite ...	MgCO_3 native	D.C.
Malacite green ...	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Fus.
Manganese ...	Mn ...	55	1225
Manganese dioxide.	MnO_2 ...	87	
Manganous oxide ...	MnO ...	71	
Marble ...	CaCO_3 ...	100	D.C.
Minium ...	Pb_3O_4 ...	685	
Muscovite ...	$\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$...	796	
Nickel ...	Ni ...	58.7	1452
Nickel oxide ...	NiO ...	74.7	
Nitre potash.	KNO_3 ...	101	
Nitre-soda ...	NaNO_3 ...	85	
Orthoclase ...	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$...	558	1200
Pearl ash ...	K_2CO_3 ...	138	909
Potash chromate ...	K_2CrO_4 ...	194	
Potash dichromate...	$\text{K}_2\text{Cr}_2\text{O}_7$...	294	400
Potash oxide ...	K_2O ...	94	
Pyrolucite ...	MnO_2 Native ...	87	Inf.
Quartz ...	SiO_2 Cryst ...	60	Inf.
Realgar ...	As_2S_3 ...	246	

Name	Formula	Mol. wt.	M.P.°C
Red lead ...	Pb_3O_4 ...	685	
Rutile ...	TiO_2 ...	80	1700
Saltpetre ...	KNO_3 ...	101	
Selenite ...	Gypsum
Selenium ...	Se ...	79	217
Siderite ...	$FeCO_3$ native ...	115.8	D.
Silica ...	SiO_2 ...	60	1680
Silicic acid ...	H_2SiO_3 ...	78	1710
Silimanite ...	$Al_2O_3 \cdot SiO_2$...	162	1800
Silver ...	Ag ...	108	960
Soapstone ...	Talc
Soda ...	Na_2O ...	62	
Soda ash ...	Na_2CO_3 ...	106	860
Sodium chloride ...	$NaCl$...	58.5	819
Soda crist ...	$Na_2CO_3 \cdot 10H_2O$...	285	60
Sodium chromate ...	$Na_2CrO_4 \cdot 10H_2O$...	342	
Sodium dichromate ...	$Na_2Cr_2O_7 \cdot 2H_2O$...	298	
Sodium silicate ...	$Na_2O \cdot SiO_2$...	122	1056
Stannic chloride ...	$SnCl_4$...	261	
Stannic oxide ...	SnO_2 ...	151	1127
Steatite ...	Talc
Talc ...	$3MgO \cdot 4SiO_2 \cdot H_2O$...	378	
Tin ...	Sn ...	119	232
Tincal ...	Native borax
Titanium ...	Ti ...	48	1825
Titanium oxide ...	TiO_2 ...	80	1560
Uranium ...	U ...	238	800
Uranium oxide ...	UO_2, U_3O_4 ...	270, 779	
White lead ...	$2PbCO_3 \cdot Pb(OH)_2$...	775	D.C.
Whiting ...	$CaCO_3$ Soft native ...	100	D.C.
Willemite ...	$2ZnO \cdot SiO_2$...	222	I. F.
Witherite ...	$BaCO_3$ native ...	179.4	D.C.
Wollastonite ...	CaO, SiO_2 Native ...	116	1540
Zinc ...	Zn ...	65.4	419
Zinc oxide ...	ZnO ...	81	
Zinc sulphate ...	$ZnSO_4 \cdot 7H_2O$...	122	
Zircon ...	$ZrSiO_4$...	183	
Zirconia ...	ZrO_2 ...	122	3000

TABLE 3. British standard sieves. (I. M. M.)

Sieve No.	Diameter of aperture.		Sieve No.	Diameter of aperture	
	Inches.	M. M.		Inches.	M. M.
5	0.1	2.54	70	0.0071	0.18
8	0.0625	1.587	80	0.0063	0.160
10	0.05	1.27	90	0.0055	0.139
12	0.0416	1.059	100	0.005	0.127
16	0.0313	0.795	120	0.0042	0.107
20	0.025	0.635	140	0.0036	0.091
30	0.0167	0.424	160	0.0031	0.079
40	0.0125	0.317	180	0.0028	0.071
50	0.01	0.254	200	0.0025	0.063
60	0.0083	0.211	250	0.002	0.051

Conversion formula.

British mesh = $\sqrt{\text{conti-mesh} \times 2.54}$

Continental mesh = $(\text{British mesh})^2 \times 0.155$.

TABLE 4. Some useful data.

Lineal measure.

220 yds.	=1 Furlong.
8 Furlongs	=1 Mile.
3 Miles	=1 League.
1 Kilometer	=0.621 Miles.
1 Metre	=39.37 Inches.
1 Inch	=2.54 Cms.

Volume measures.

1 Gallon	=268.8 Cu. Inches.
	=8 Pints.
	=4.546 Litres.
1 Cu. Foot	=6.23 Gallons.
1 Litre	=1.76 Pints.
	=61.03 Cu. Inches.
1 Cu. Centimeter	=0.061 Cu. Inches.
1 Cu. Metre	=1.308 Cu. yds.

Weights.

1 Gram	=15.432 Grains.
1 Ounce	=28.35 Grams.
16 Ozs.	=1 Pound.
	=453.59 Grams.
14 Pounds	=1 Stone.
112 Pounds	=1 Hundred weight.
2240 Pounds	=1 Ton
1 Kilogram	=2.235 Pounds.
1 Ton	=1016.05 Kilo grams.

Surface Area.

1 Acre = 4840 sq. yards.

640 Acres = 1 sq. Mile.

1 Sq. Inch = 6.45 Sq. Cms.

1 Sq. Meter = 1550 Sq. Inches.

Miscellaneous.

1 Gallon of Water = 10 lbs.

1 Pint of water = 20 ozs.

1 Cu. ft. of Water = 62.278 lbs.

1 Cu. ft. of Earth, Comn = 136 lbs.

1 Cu. ft. of Fire clay = 85 lbs.

1 Cu. ft. of Shale = 162 lbs.

1 Cu. ft. of Sand Comn = 104 lbs.

1 Cu. ft. of Quartz = 166 lbs.

WHITE TIN OXIDE (99.5-100%)

For all purposes where purity is essential.

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